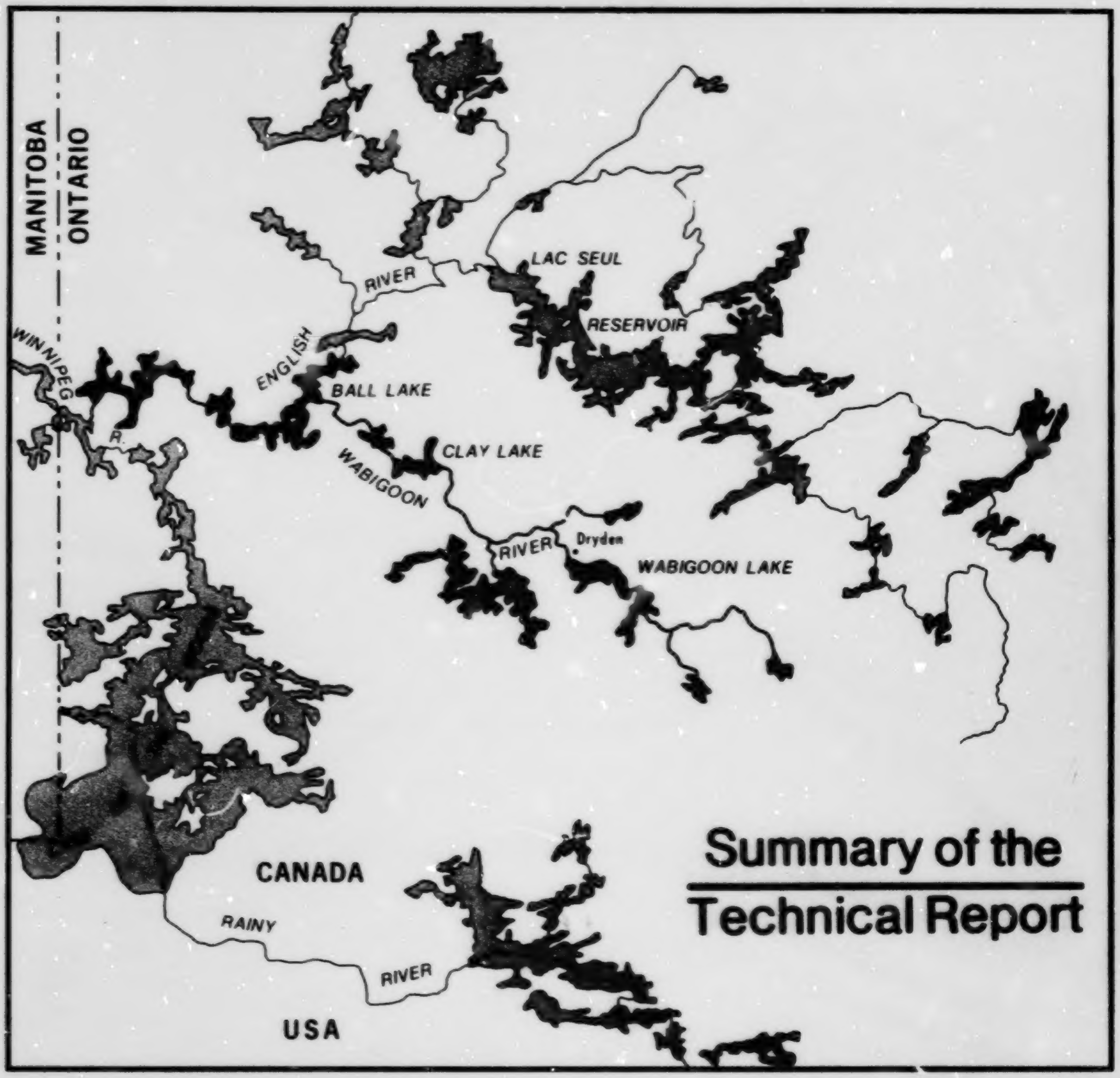
Mercury Pollution in the Wabigoon-English River System of Northwestern Ontario, and Possible Remedial Measures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Dryden
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CANADA
RAINY
RIVER
USA

Summary of the Technical Report

Government of Canada

Government of Ontario

84- 4633 /

MERCURY POLLUTION IN THE WABIGOON-ENGLISH RIVER SYSTEM OF NORTHWESTERN ONTARIO, AND POSSIBLE REMEDIAL MEASURES

SUMMARY OF THE TECHNICAL REPORT

Prepared by

The Canada-Ontario Steering Committee

1983

From: The Wabigoon-English River Mercury Study Steering Committee

To: The Honourable Charles Caccia, P.C.,M.P.
Minister of the Environment
Ottawa

The Honourable Andrew S. Brandt, M.P.P.
Ontario Minister of the Environment
Toronto

The Honourable Alan W. Pope, M.P.P.
Ontario Minister of Natural Resources
Toronto

Gentlemen:

The Steering Committee of the Canada-Ontario Wabigoon-English River Mercury Study is pleased to submit, herewith, its final report on Mercury Pollution in the Wabigoon-English River System of Northwestern Ontario, and Possible Remedial Measures. The report consists of two volumes. Volume 1 is a Summary which highlights the Problem, the Conclusions of the research and monitoring studies and the Recommendations agreed to by the Steering Committee. Volume 2 is the complete Technical Report and includes all of the details of the individual studies carried out under the Canada-Ontario Agreement Respecting Mercury Pollution in the Wabigoon-English River System.

Respectfully submitted, February 1984.

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PREFACE

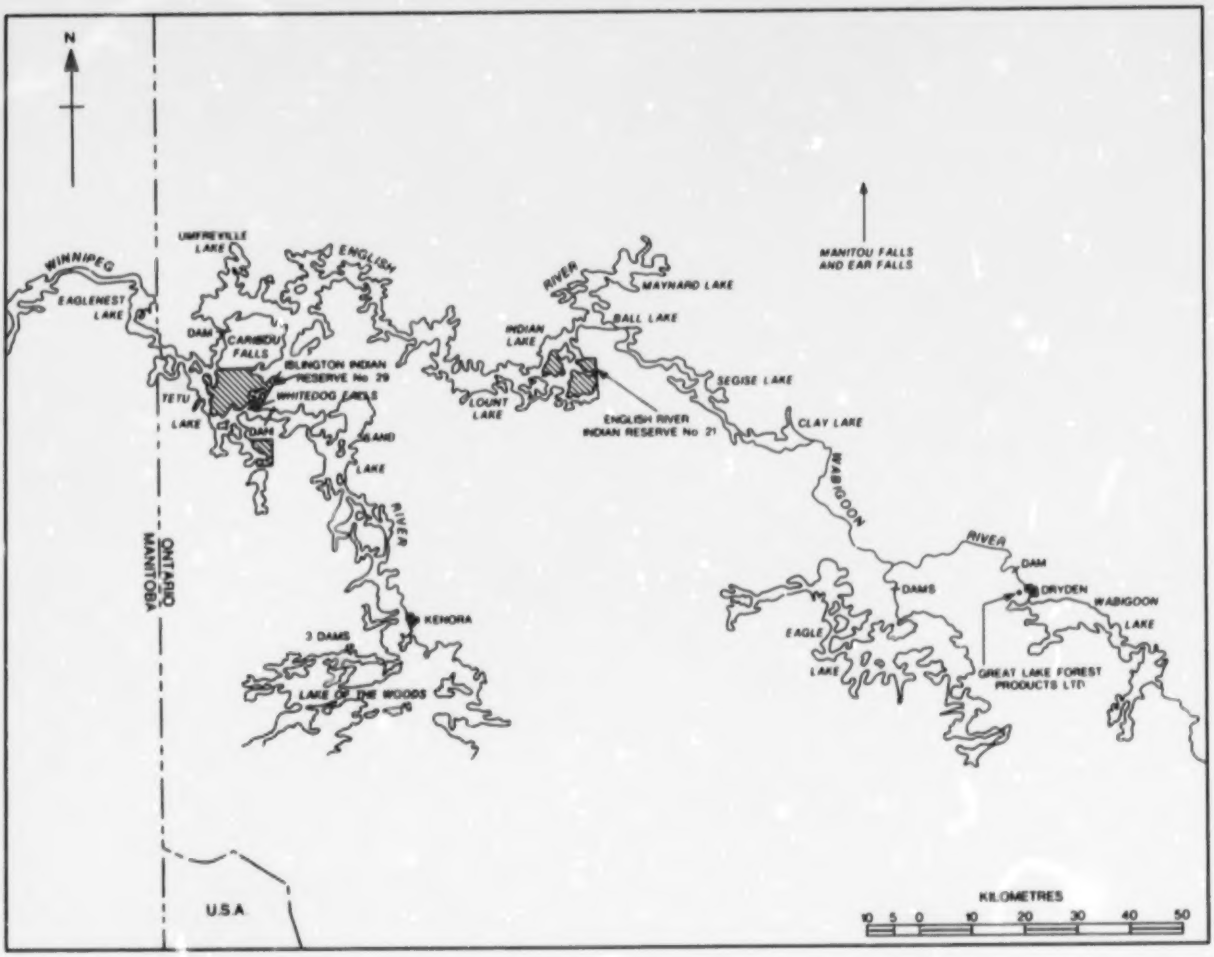
This Summary Report has been prepared by the Canada-Ontario Steering Committee of three federal and three provincial staff, established to investigate mercury pollution in the Wabigoon-English River system of northwestern Ontario. The report highlights the Problem, Conclusions and Recommendations associated with the assessment of mercury pollution in the system and with the evaluation of methods which might be employed to accelerate natural recovery of the system. The material has been extracted largely from the companion Technical Report which is a detailed compilation of the results of investigations conducted in the field by individual researchers. Some sections of the Technical Report have already appeared in scientific journals. Although they have been derived from a review of the Technical Report, the Conclusions and Recommendations are those of the Steering Committee and do not necessarily represent a consensus of the authors of the Technical Report.

ACKNOWLEDGEMENTS

The Steering Committee wishes to acknowledge the assistance of two individuals who have played a major role in this study but whose names are not to be found in either the Summary or Technical Report.

The first is Dr. A.L. Hamilton, presently with the International Joint Commission in Ottawa, who played an important role in initiating government interest in the mercury pollution issue in the Wabigoon River. He has followed the study to its completion, has provided the Steering Committee with critiques of the Technical Report, and has helped to resolve differences of interpretation between the scientific teams.

The second is Mr. W.A. Creighton who has played an important role in managing the provincial part of the study. Mr. Creighton has been an active participant at all Steering Committee Meetings and the final Technical Report has benefitted from his input.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WINNIPEG
EAGLENEST LAKE
ENGLISH
RIVER
DAM
CARIBOU FALLS
ISLINGTON INDIAN RESERVE No 29
WHITEDOG FALLS
TETU LAKE
DAM
SAND LAKE
RIVER
ONTARIO
MANITOBA
KENORA
3 DAMS
LAKE OF THE WOODS
U.S.A.
INDIAN LAKE
LOUNT LAKE
MAYNARD LAKE
BALL LAKE
ENGLISH RIVER INDIAN RESERVE No 21
SEGISE LAKE
CLAY LAKE
WABIGOON
RIVER
MANITOU FALLS AND EAR FALLS
DAM
DRYDEN
WABIGOON LAKE
DAMS
EAGLE LAKE
GREAT LAKE FOREST PRODUCTS LTD
KILOMETRES
10 5 0 10 20 30 40 50

FIGURE 1: LOCATION MAP, ENGLISH - WABIGOON LAKE SYSTEM

INTRODUCTION

The Wabigoon-English River system in northwestern Ontario and eastern Manitoba is one of the more severely mercury polluted waterways of the world (Armstrong and Hamilton 1973). The Ojibway communities of Grassy Narrows and White Dog are located on the banks of the English River downstream from Ball Lake and at the confluence of the English and Winnipeg Rivers respectively. The people of these Bands used to fish the waters of the river-lake system for commercial purposes but also to supplement their own food supply. They were also employed as guides to sport fishermen, mainly from the United States. The economy of the region depends heavily on the pulp and paper industry and tourism, mainly related to wilderness sport fishing, and thus a conflict has arisen in water resource use. This report is primarily concerned with the mercury pollution in the river system and its associated lakes, and with the evaluation of methods which might be employed to accelerate natural recovery of the system. A brief description follows of the river-lake system, a historical sketch of the pollution problem, and the consequences to the native communities.

In northwestern Ontario (Fig. 1), the Wabigoon River leaves Wabigoon Lake and flows through the town of Dryden. The river widens about 53 miles further downstream to form Clay Lake, later entering Ball Lake where it joins the English River. In turn, the English River flows through a chain of lakes and finally merges with the Winnipeg River which empties into the south basin of Lake Winnipeg, more than 160 kilometres west of Dryden. This vast river-lake system stretches across a sparsely populated land of boreal forest, low relief, and Precambrian granitic and greenstone belts overlain by patches of clay and sandy till.

The principal source of pollution in the river-lake system is a paper mill complex presently operated by the Dryden Mill Division of the Great Lakes Forest Products Company (formerly owned by Reed Ltd.). The paper mill has been discharging organic wastes into the Wabigoon River since its construction in 1913 (German, 1969). Consequently, some sections of the riverbed between Dryden and the village of Quibell, near the inflow to Clay Lake, are covered with putrefying wood fragments. Floating masses of foam together with heavy loads of suspended debris were common but current conditions in the river are greatly improved as a result of primary and secondary treatment of mill wastes. Effluent from the Dryden municipal sewage treatment plant is also released into the river after primary and secondary treatment.

The mercury pollution was derived mostly from the effluents of a chlor-alkali plant (Armstrong and Hamilton, 1973; Fimreite and Reynolds, 1972; Troyer, 1977) which operated from 1963 to 1975. From 1963 to 1970, unrestricted quantities of mercury, approximately 9-11 metric tonnes in total, were released into the river. In 1970 when the Ontario Water Resources Commission became aware of the problem, action was taken which reduced the mercury discharge by about 99 per cent. In 1975, the chlor-alkali plant was converted to a process which does not use mercury; however, effluent from the mill complex still contains small and variable concentrations of mercury (5-10 kg per year). Primary treatment of mill wastes installed in September 1980 was not very effective in reducing residual traces of mercury in mill effluent (approximately 20% removal). Secondary treatment which was started in 1983 may effect some further removal of mercury.

Armstrong and Hamilton (1973), Parks (1976), and Jackson (1979) determined the distribution of mercury in the sediments and biota in the system. The mercury pollution has caused high mercury concentrations in fish throughout the river-lake system from Dryden at least as far downstream as the Manitoba border. The mercury concentrations were well over 0.5 parts per million (ppm) (Kenney, 1971; Scott and Armstrong, 1972; Armstrong and Hamilton, 1973; Fimreite and Reynolds, 1973; Annett et al., 1975; Bishop and Neary, 1976), the limit set by the Canada Food and Drug Directorate for edible fish marketed in Canada. Mean mercury levels in pike were consistently greater than 2.0 ppm, all the way from Clay Lake (the first lake downstream from Dryden) to Tetu Lake at the confluence of the English and Winnipeg Rivers. Mercury concentrations in pike in local lakes which are not part of the Wabigoon-English system range from less than 0.5 to 2.0 ppm (Bishop and Neary, 1976). Other aquatic organisms such as crayfish have also been affected (Armstrong and Hamilton, 1973; Vermeer et al., 1973; Annett et al., 1975). Shortly after mercury discharges were reduced, mercury concentrations in biota declined rapidly (Armstrong and Scott, 1979), but the rate of decrease subsequently slowed and mercury concentrations in fish still remain well above recommended levels for unrestricted human consumption.

Commercial fishing was banned in 1971; however, sport fishing continued to be permitted. The Ontario Government provided information and recommendations to the public on mercury concentrations in fish and on restricted consumption of contaminated fish, (Guide to Eating Ontario Sport Fish-Northern Ontario, which is updated annually by the Ministry of Environment and Ministry of Natural Resources).

Mercury pollution has had serious direct and indirect effects on native populations in the region, especially the Ojibways of the Grassy Narrows and White Dog bands. Ojibways employed as guides by owners of fishing lodges catering to sportsmen were exposed to more mercury and possible chronic mercury poisoning owing to their practice of frequently joining their customers in the consumption of shore lunches of freshly-caught fish.

Ever since the potential danger from mercury poisoning became apparent, the Band members have been urged to stop eating the contaminated fish and the Ontario Government has been providing the communities with uncontaminated frozen fish.

Medical surveys conducted between 1971 and 1978 (Health and Welfare Canada, 1973; Clarkson, 1976; Wheatley, 1979) have shown some individuals in both-bands had blood mercury levels exceeding 100 parts per billion (ppb), even in winter when blood levels should be lowest owing to reduced consumption of fish. At blood levels above 100 ppb, a human adult is considered to be at risk (Wheatley et al., 1979). The higher levels were in the range of 100-500 ppb. The maximum value recorded was 600 ppb.

Symptoms of methyl mercury poisoning (or Minamata disease) may be detected first in the most sensitive 5% of adults whose blood levels are in the range 200-500 ppb. Unborn children, however, are more sensitive than adults (Wheatley, 1979; Wheatley et al., 1979). Out of the 40 at risk individuals in Northwestern Ontario who submitted to clinical examination, none was found to have unequivocal symptoms of mercury poisoning as of December 31, 1978, although 10 of them had neurological abnormalities which were possibly attributable to it. Uncertainty regarding cause arises from the fact that symptoms of mild forms of Minamata disease are similar to those of various other conditions, thus making conclusive diagnosis difficult (Wheatley, 1979; Wheatley et al., 1979).

Although the scientific community had produced considerable information about mercury pollution of the Wabigoon-English system, it was not possible to accurately estimate the system's rate of recovery. Therefore, concern about the mercury problem and its continuing effect on commercial fishing, angling and tourism on the Wabigoon and English Rivers led to an Agreement between the Federal and Ontario Governments for joint funding under the Canada Water Act to undertake a $300,000 study to develop a better understanding of the problem. Sources, pathways and fate of total and methylmercury were determined. A better understanding of the mechanisms by which mercury enters fish was expected to lead to the development of remedial measures to reduce mercury contamination and speed the recovery of the river-lake system. The specific objectives of the Agreement were as follows. *"To carry out shared-cost and other projects to evaluate and determine the effectiveness of various mercury amelioration measures in the Wabigoon-English River System, and to include:*

(1) a review of all data on sediment, water and biota mercury levels to determine the adequacy of existing information; and, depending on the findings thereof, a survey of pathways, transport, rates of accumulation and distribution of mercury in the Wabigoon-English River System; and

(2) a review of all available information to determine the factors affecting the availability of mercury for uptake by biota, and, depending on the results thereof, experiments to measure the effectiveness of alternative ways of reducing the availability of mercury in the Wabigoon-English River System."

CONCLUSIONS

The following major conclusions have, to a large extent, been extracted from the comprehensive Technical Reports. Conclusions of a more general nature are in bold print and are followed by more specific conclusions relevant to them.

The specific conclusions documented have been developed by an analysis of data from the river-lake systems, limnocorral enclosures and laboratory research.

I. **The Wabigoon-English River system is gradually improving but, in the absence of intervention, mercury levels in fish are expected to remain unacceptably high for many years. The degree of improvement of mercury levels in fish which would result from remedial action could not be determined from the study results, but the nature of the improvement would be to accelerate the rate of recovery, compared to the natural changes occurring in the system. Mercury levels in biota decline less dramatically with distance downstream from Dryden than do mercury concentrations in sediments. This appears to be related to an increased bioavailability of mercury with increasing distance downstream from Dryden.**

   i) Most biota in the system show that there has been a rapid and significant drop in mercury concentration between the early seventies and eighties (Figs. 2, 3 and 4). In the ten years since mercury effluents were treated and controlled, the system has shown a more rapid return toward natural conditions than was envisaged in the middle seventies.

   ii) There has been a decrease in mercury concentrations in crayfish since 1970 but most of this decrease took place from 1970 to 1973 and concentrations are now declining at a slower rate (Fig. 2).

   iii) Mercury concentrations in adult pike (Fig. 3) and walleye (Fig. 4) have decreased since the middle seventies and these declines are expected to continue, but at reduced rates.

   iv) It is anticipated that when the oldest fish, with the highest mercury concentrations, die within the next few years, the calculated mean mercury levels of the walleye population will drop further and become more representative of the present mercury pollution status of the system. There is a lag between the pollution status in terms of surface sediment mercury concentrations and the mercury concentration in the oldest fish which may have accumulated their mercury several years ago.

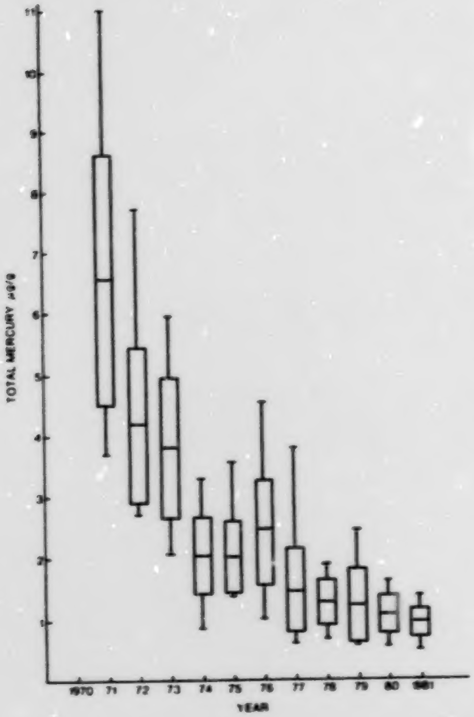

FIGURE 2 MEAN, STANDARD DEVIATION AND RANGE OF MERCURY CONCENTRATIONS IN ABDOMINAL MUSCLE OF CRAYFISH OVER 65 mm IN TOTAL LENGTH, CLAY LAKE 1970-1981 (G.P. McRAE, FRESHWATER INST. WPG.)

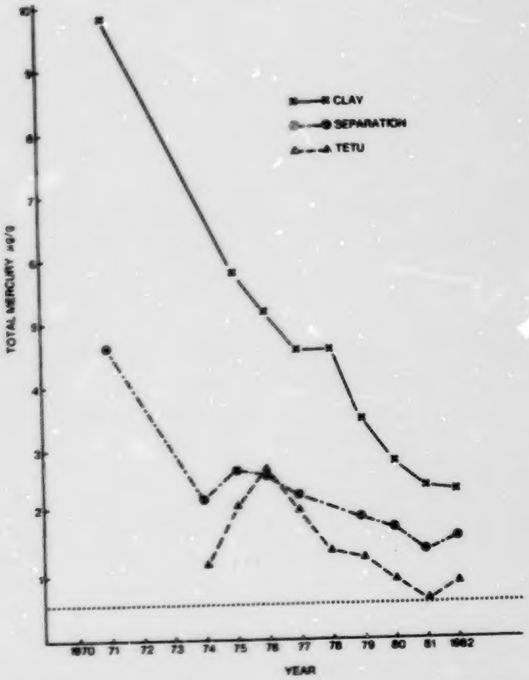

FIGURE 3 MERCURY CONCENTRATIONS IN 60 cm NORTHERN PIKE FROM THREE LAKES IN THE WABIGOON/ENGLISH/WINNIPEG RIVER SYSTEM, 1971-1982 (AFTER BISHOP AND NEARY, 1978). DOTTED LINE REPRESENTS MEAN OF FOUR ON SYSTEM CONTROL SITES.

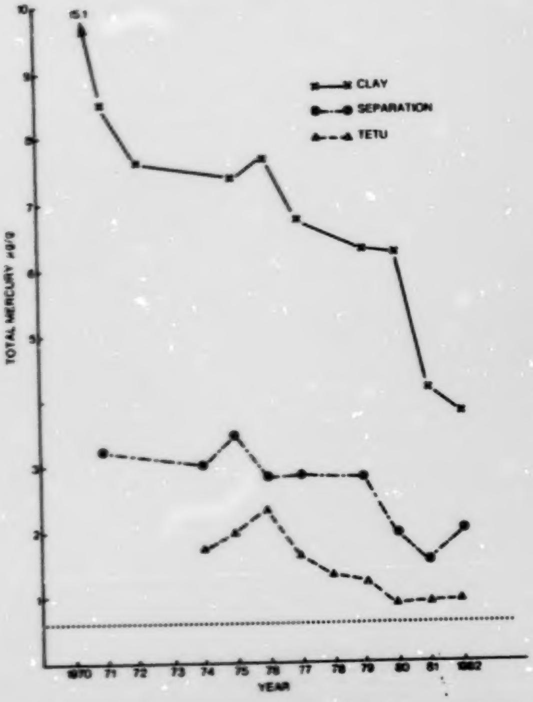

FIGURE 4 MERCURY CONCENTRATIONS IN 50 cm WALLEYE FROM THREE LAKES ON THE WABIGOON/ENGLISH/WINNIPEG RIVER SYSTEM 1970-1982 DOTTED LINE REPRESENTS MEAN FOR FOUR CONTROL LAKES

v) In the last two years, sufficient declines in mercury levels in the three key sport fish species - northern pike (Fig. 3), walleye (Fig. 4) and whitefish have permitted the publication of less restrictive consumption advisories. Improvements, in terms of species and sizes of fish suitable for limited or unrestricted consumption are the greatest in Tetu Lake in the western portion of the basin. In fact, in comparison to fish data from other waterbodies in nearby areas unaffected by the industrial discharges, mercury concentrations in Tetu Lake fish appear to be approaching background levels. Moving closer to Dryden through Separation and Ball Lakes, consumption advice becomes very restrictive, but again, the trend toward improving conditions can be observed.

vi) Mercury concentrations in fish in Clay Lake, the downstream lake closest to Dryden, are so high that most sport fish are unacceptable for human consumption. However, even in this waterbody, mercury levels in fish have declined (Figs. 3 & 4).

vii) Mercury methylation in the system is driven mainly by microbiological processes.

viii) For the first time mercury methylation has been documented in the water column and in fish intestines. In the fish, this is proportional to intestinal mucus content. Thus, there are two sources of methylmercury in addition to the previously known source from bottom sediments.

ix) Mercury concentrations in biota are related to total mercury (mercury in all forms) concentration and methylmercury (mercury combined with the organic methyl group and regarded as the most toxic form) concentrations in the water column.

II. Measures to increase the water column load of clean lake-derived sediments would accelerate the rate of sedimentation and in turn would lead to decreased mercury concentrations at the sediment-water interface. In addition to reductions in the release of mercury from bottom sediments, the increased suspended sediment load in the water column would reduce the bioavailability of mercury in the water column. Both can be brought about by dredging and resuspending uncontaminated, clay-rich lake sediments.

i) In enclosures, clay sediments reduced mercury in biota by ten times (Fig. 5) compared to two times for selenium and not at all when primary productivity was increased. Resuspended clay-rich lake sediment in enclosures bound mercury much better than the clay from river banks. This may be related to organics (probably "dissolved" organic matter of less than 0.45 μ size) and iron and manganese oxide coatings in the sediments. Mercury remains in the water column because it is associated with particles of small size, but this mercury is not bioaccumulated.

ii) Particulate mercury in the water column was over 98% unextractable by a series of mild reagents and may not be readily "bioavailable".

iii) Mercury in silt was more readily solubilized, and probably more methylated, than mercury in wood chip sediments which are more prevalent close to the industrial complex at Dryden.

iv) Increasing suspended sediment up to 18 mg/L in enclosure experiments did not decrease primary production or fish growth.

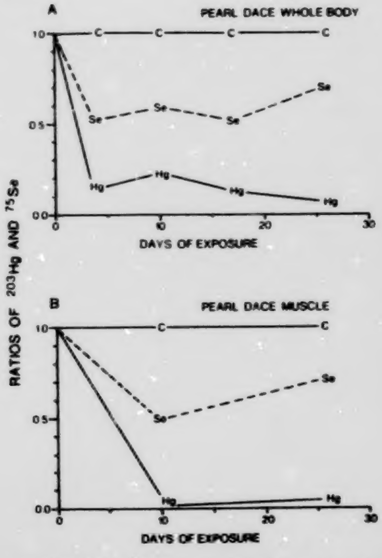

FIGURE 5 INHIBITION OF 203-MERCURY (Hg) AND 75-SELENIUM (Se) BIOACCUMULATION IN PEARL DACE WHOLE BODY (UPPER PANEL) AND MUSCLE SAMPLES (LOWER PANEL) BY ADDITION OF INORGANIC RICH SEDIMENT TO AN ENCLOSURE. THE DATA ARE EXPRESSED AS RATIOS OF ^{203}Hg AND ^{75}Se ACTIVITIES IN THE SUSPENDED SEDIMENT ENCLOSURE DIVIDED BY ACTIVITIES IN THE COMBINED CONTROL ENCLOSURES (C)

III. Sources of mercury in bottom sediments in any specific lake or river bottom area contribute to the mercury problem at any one location in the short term (months) but in the longer term (years) the upstream sources are of continuing importance. The part of the system downstream from Dryden to the inlet of Ball Lake remains very contaminated by any world standard. However, from the outlet of Ball Lake to the Manitoba border the problem is less severe.

i) Present mill discharges do not appear to be an important source of mercury with respect to Clay Lake and downstream.

ii) Dissolved methylmercury concentrations, and total methylmercury loadings increased downstream in the Wabigoon River from Dryden to Clay Lake.

iii) Between Dryden and the Eagle River confluence, particulate mercury and methylmercury, total soluble mercury and total mercury concentrations in the water were all greatest during the spring flood due to resuspension of contaminated bottom sediments and their downstream transport.

iv) Between Dryden and Clay Lake, the soluble methylmercury concentration was low during the spring but high during the summer.

v) Water mercury concentrations are influenced more by surface than by deep bottom sediments.

IV. **The concentration of mercury and its chemical and physical forms in the water column are affected by several variables especially temperature, oxygen, suspended sediment concentrations, and microbial activity. At any given site the partitioning of mercury among surface sediments, water and suspended solids characteristically stabilizes within days; however, there likely are losses from the water surface to the atmosphere which were not measured during the investigations. In this contaminated system the most important source affecting mercury in the water column is the mercury concentration in the surface sediment. The form of mercury influences its bioavailability.**

i) Sediments are now the main source of mercury to the water at least from Dryden to below Ball Lake.

ii) Temperature affects mercury concentration in the water at a given time and place (Fig. 6).

iii) The water reaches a maximum mercury concentration for a given temperature within a few days. Mercury release from sediments likely continues as the result of microbial activity but the concentration in the water does not change; thus it appears that mercury is being lost to the atmosphere.

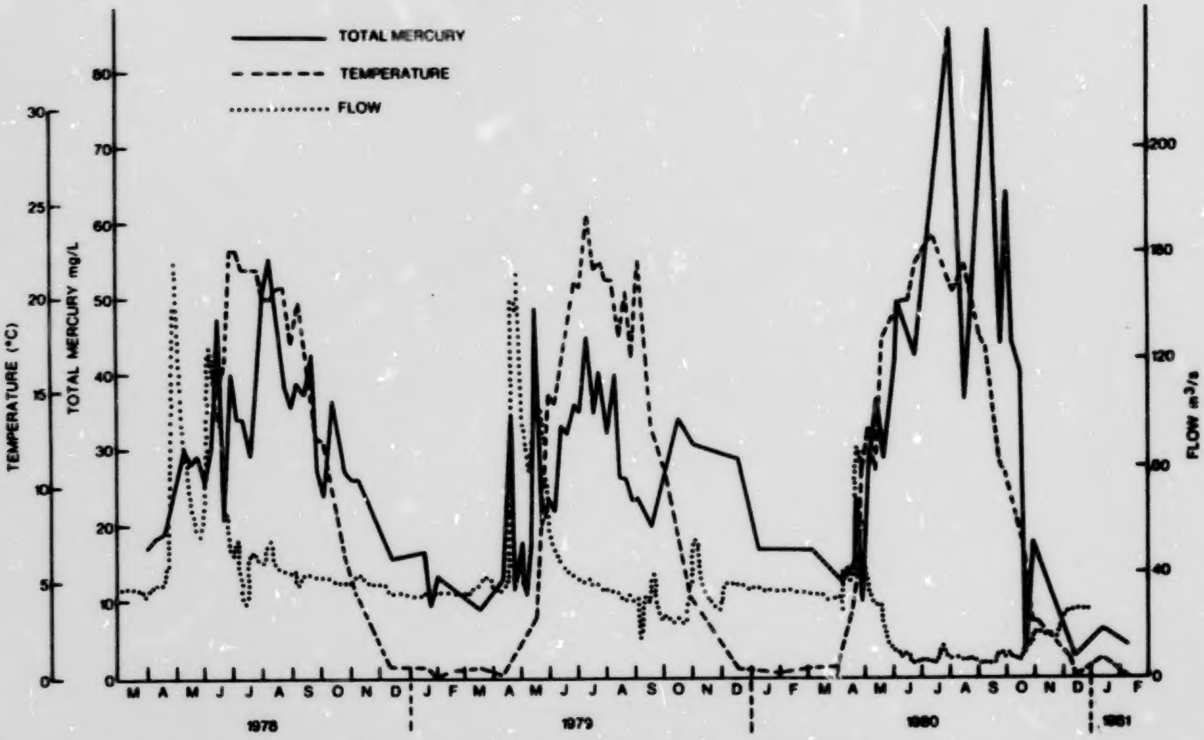

FIGURE 6 TOTAL MERCURY AND TEMPERATURE DATA, INFLOW TO CLAY LAKE. FLOW AT QUIBELL. MARCH 1978 TO FEBRUARY 1981

iv) In summer, when water temperatures were elevated and during the absence of resuspended particulates, dissolved methylmercury was related to total dissolved mercury in the water. In the spring when sediments were resuspended, dissolved and suspended methylmercury did not relate to total mercury concentrations.

v) The ratio of methyl to total mercury concentration in surface sediments increases with increasing distance from Dryden. The ratio of methyl to total mercury in water also increases down the system but the average concentrations of methyl and total mercury generally decrease. The one exception is the increase in methylmercury concentration across Clay Lake.

vi) Methylmercury concentrations in the water are a varying function of total mercury concentrations, with the ratio of one to the other changing down the system (Fig. 7).

vii) Methylmercury and mercury were bound to sediment in different ways. Methylmercury was associated with sulphur and with iron oxides. Mercury was associated with humid-iron material and with easily-extractable iron and manganese.

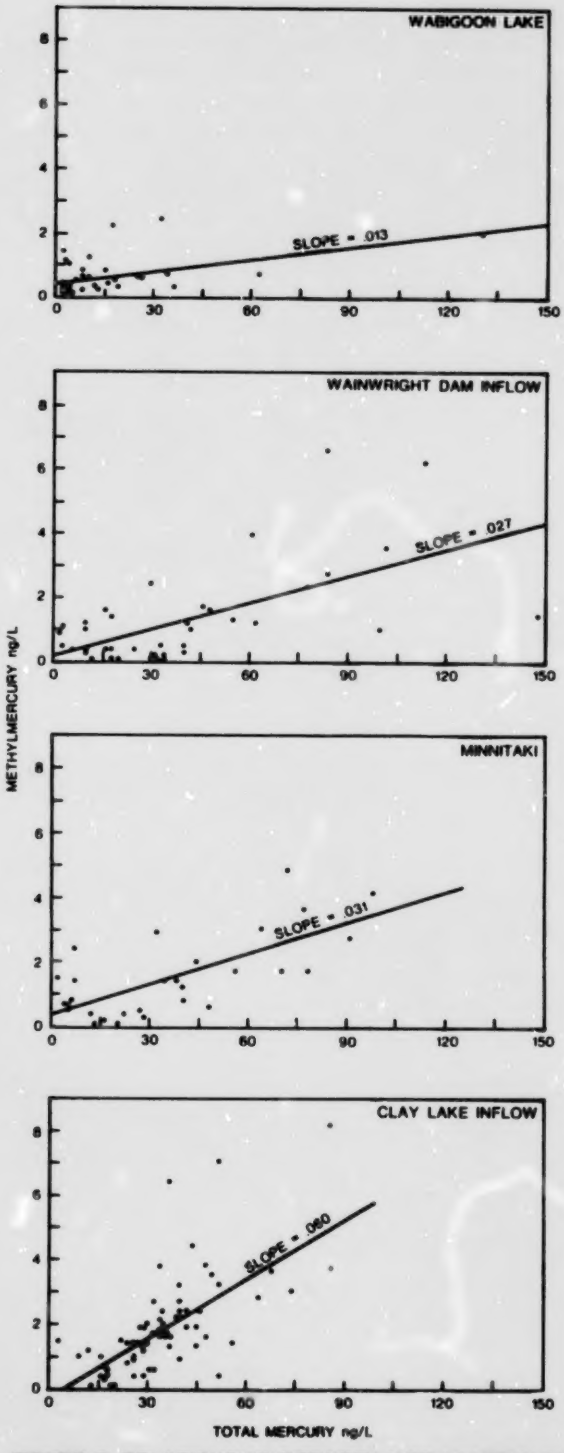

FIGURE 7: RELATIONSHIP BETWEEN METHYLMERCURY AND TOTAL MERCURY FOR NON-HIGH FLOW PERIODS, WABIGOON LAKE - CLAY LAKE, 1978 - 1980.

V. A number of other amelioration procedures were explored as part of this study. Selenium was investigated as a possible agent for mercury amelioration. Literature reports indicate that mercury is less toxic to the consumers of fish if it is associated with selenium. The experiments were designed to see whether or not selenium would be taken up by the fish along with the mercury. While selenium supplementation seems to be effective, more research is required before its use could be seriously considered. Other techniques found to be less suitable included: addition of sulphate which was intended to immobilize mercury in sediments as insoluble mercuric sulphide; and addition of algal nutrients which was intended to enhance fish growth thereby reducing the mercury concentrations of fish by dilution. Ploughing of surface sediments to reduce mercury concentrations was not attempted because of expected technical difficulties.

i) The mercury to selenium ratio in fish is high, due to high mercury concentrations, but also due to abnormally low selenium concentrations in this system.

ii) A 100 ppb concentration of selenium in water reduced mercury uptake in fish by 50% (Fig. 8). This effect is transmitted via the food web rather than by the water.

iii) Mercury reduction in sport fish could be expected from increased selenium concentrations in water. Some reduction can occur even at selenium concentrations as low as 1 ppb (Fig. 8).

iv) Toxicity tests as a literature review indicate a low safe concentration for selenium. The Canadian drinking water guideline is 10 ppb.

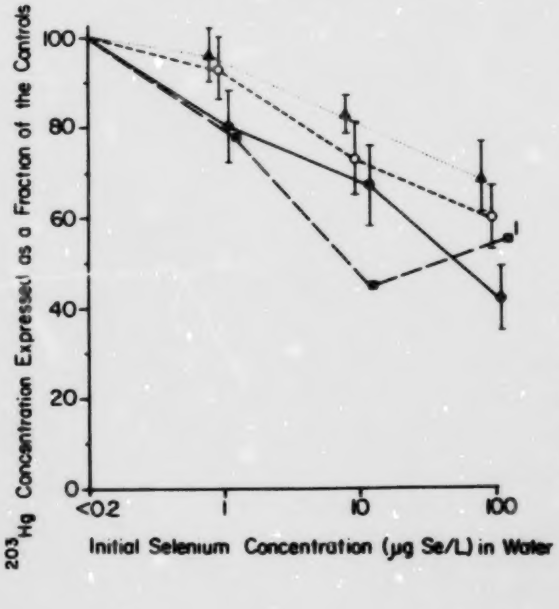

FIGURE 8

MERCURY-203 ACCUMULATION IN WHOLE BODIES OF ADULT CRAYFISH (○), ADULT PEARL DACE (▲), YOUNG-OF-THE-YEAR YELLOW PERCH (●), AND JUVENILE WHITE SUCKER (■) IN THE Se ENCLOSURES. DATA ARE EXPRESSED AS RATIOS IN WHICH ^{203}Hg ACTIVITIES IN Se-EXPOSED ANIMALS ARE DIVIDED BY THE MEAN ACTIVITIES OF THE COMBINED CONTROLS. MEANS (±SE) OF THE SEVERAL SAMPLING PERIODS (CRAYFISH 4, DACE 6, PERCH 4, AND SUCKER 1) ARE PRESENTED FOR EACH ORGANISM. ONLY ONE SUCKER WAS RETRIEVED FROM THE 100 µg Se/L ENCLOSURE (SUPERSCRIPT 1)

RECOMMENDATIONS

The recommendations which follow are listed in order of priority for action. They have been limited to those which can be arrived at on the basis of the conclusions described previously. These, in turn, are supported by the Technical Report which contains many other important conclusions. Our recommendations are limited to those remedial actions judged to be technically feasible in bringing about some amelioration of the mercury pollution status of the river. We expect that they would result in a more rapid recovery of the system, but the degree of expected improvement of mercury levels in fish could not be determined quantitatively.

Clearly, although the pollution is the disease, the symptoms are primarily the impact on the Native populations, local fishermen, sport fishermen and fishing lodge owners.

We are aware that the use of funds for amelioration may not, in the larger context, be the most worthwhile response to the problem. In particular, there is clear evidence that the system continues to exhibit natural recovery.

The recommendations of the Committee are:

I. THAT THE MERCURY MONITORING AND THE FISH CONSUMPTION GUIDELINE PROGRAM BE CONTINUED

Annual sampling and testing of fish from the four routinely tested waters (Clay, Ball, Separation and Tetu Lakes) should be continued. Testing of sport fish in all other previously tested "on-system" and "off-system" lakes in the Wabigoon-English system should be undertaken in the next two years to update all previous consumption advisories and evaluate mercury trends in other parts of the system.

II. A PILOT PROJECT FOR SEMI-CONTINUOUS RESUSPENSION OF NON-MERCURY CONTAMINATED SEDIMENT INTO THE SYSTEM AT CRITICAL POINTS BE CONDUCTED AND ASSESSED

On the basis of the conclusions, the resuspension of lake-derived sediments represents a promising technique for the rehabilitation of the Wabigoon-English River System. However, there are a number of factors which may affect the successful implementation of this technique in a complicated lake/river system like the Wabigoon-English.

A pilot project to semi-continuously resuspend sediments could be conducted using:

(a) Deep sediments from Wabigoon Lake injected into the Wabigoon River;

(b) Deep sediments from eastern Clay Lake injected into western Clay Lake and downstream;

(c) Deep sediment from the north basin of Ball Lake injected into the English River system.

Given these three site choices, we propose that option (b) has the greatest potential for environmental response in terms of monitoring changes in mercury concentration in fish and thus proving the technique to be successful. Resuspension would be effective in the short term by reducing bioavailability of mercury in the water column and in the long term by reducing the concentrations of mercury in surficial sediments.

If successful at site (b), we would recommend that additional sediment resuspension operations be implemented in the future at site (c) and then at site (a) above.

We wish to emphasize that the non-mercury polluted sediments which are resuspended must come from the river or lake bed and cannot be bank sediments, which have been shown to be ineffective.

It is assumed that sufficient sediment would be resuspended to reduce bioavailability of mercury in the water column and effectively reduce the surficial bottom sediment mercury concentrations.

The pilot project would be necessary both to assess the technical feasibility of the method and to provide cost estimates of applying the technique.

III. THE SEDIMENT BETWEEN DRYDEN AND CLAY LAKE BE REMOVED BY DREDGING

Sediments in the Wabigoon River, between Wabigoon Lake and Clay Lake, contain substantial quantities of mercury and will continue to be a major source of mercury in the river system.

Mercury concentrations in the water column are related to the mercury concentrations in the bottom sediments at each particular stretch of the river. Thus, upstream, contaminated sediment must be removed first in any dredging and off-river disposal plan. Thus, dreding should start at Dryden and proceed to Clay Lake. Burial of sediments in this stretch of the river is not feasible in the long term because the new sediment would be eroded and the original contaminated sediments re-exposed. Dredging operations downstream of Clay Lake are not considered to be worthwhile.

The cost of removing contaminated sediment between Dryden and Clay Lake as outlined above and confining the contaminated sediment in suitable on-land disposal areas constructed at sites near the Wabigoon River has been estimated at $19 million (1981 dollars). Some refinement of these cost estimates for dredging and confinement of contaminated sediments could be obtained by undertaking field surveys to provide better engineering design data (for example, sonar surveys, to assess river bed profiles and the number of logs in the river, soil conditions at disposal sites, etc.). These studies would have to be made prior to a final decision on the dredging option which would also be influenced by the results of the sediment resuspension project.

Although Wainwright reservoir was shown to be neither a source nor sink of mercury on an annual basis, it is a source of mercury in the spring runoff period and for effective downstream improvement, the mercury contaminated sediment in Wainwright reservoir should be completely dredged or partially dredged and a clean, deep sediment cover pumped over the remaining debris.

IV. ADDITIONAL SCIENTIFIC INVESTIGATIONS

As a result of the scientific studies which have occurred to date, two promising areas of scientific investigation were identified:

(a) Loss of Mercury to the Atmosphere

There is a distinct possibility, based on the temperature related, summer increase in mercury concentrations in river waters that mercury is being released at this time to the atmosphere. Research studies should be designed to quantify this pathway.

(b) Further Tests of the Effectiveness of Selenium on Mercury Pathways

Although, it was not as effective as suspended sediment, selenium was shown to reduce mercury uptake by biota. Selenium concentrations were also shown to be abnormally low in the system due to natural geological conditions. The necessary water concentration of selenium to have an effect on reducing mercury concentrations in biota is about 1 ppb. This concentration is well below drinking water standards and to raise the concentration to this level by adding selenite salts to the river would be by far the least costly amelioration procedure. Nevertheless, the toxicological effects on various biota in the limnocorrals and the literature review of selenium toxicity indicate that it would be unwise to pursue this amelioration technique without extensive further studies, especially whole lake experiments.

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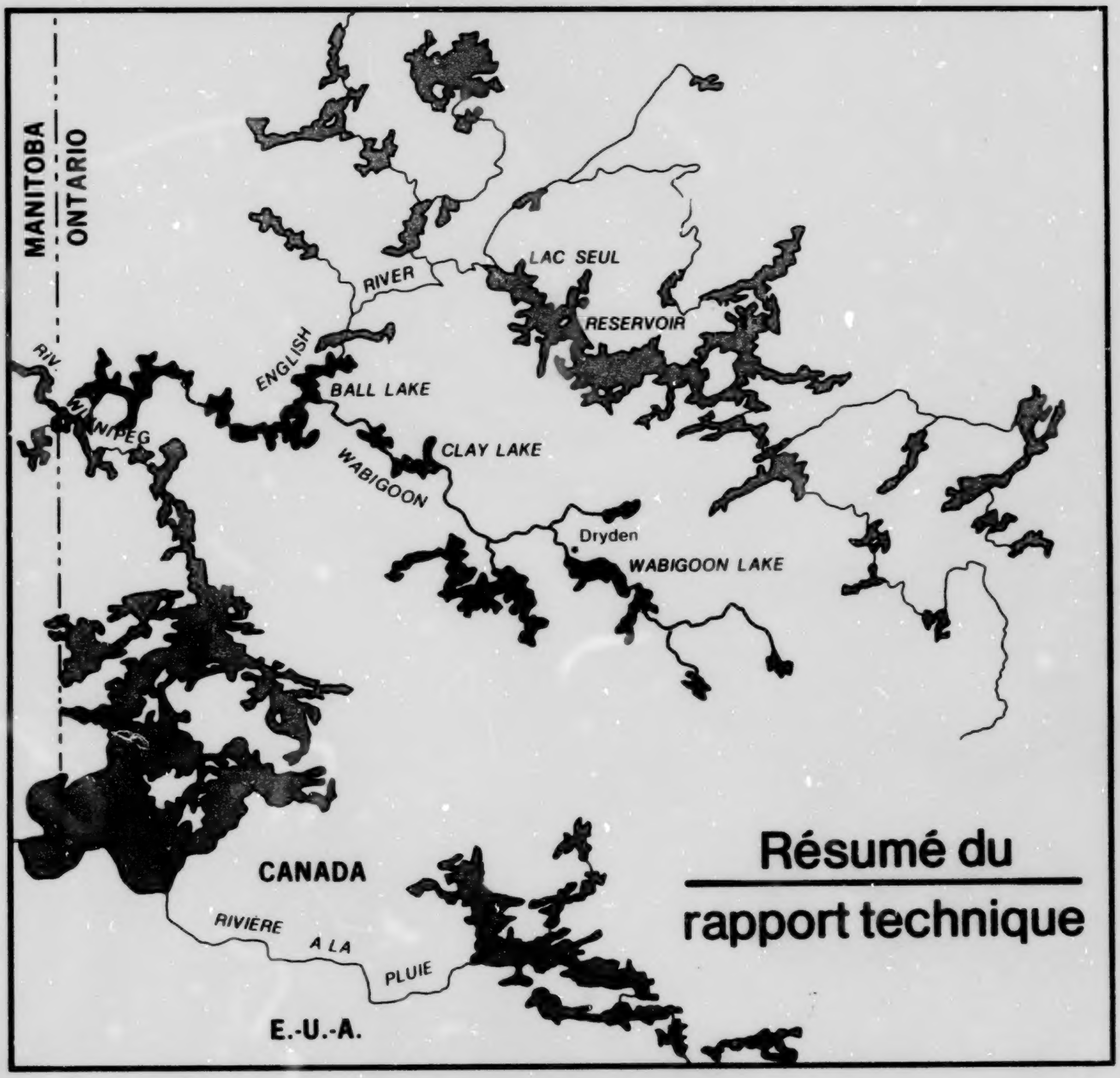
La pollution par le mercure dans le bassin hydrographique Wabigoon-Des Anglais dans le nord-ouest de l'Ontario
Diverses mesures de dépollution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Dryden
WABIGOON LAKE
CANADA
RIVIÈRE
A LA
PLUIE
E.-U.-A.

Résumé du rapport technique

Gouvernement
du Canada

Gouvernement
de l'Ontario

LA POLLUTION PAR LE MERCURE DANS LE BASSIN HYDROGRAPHIQUE WABIGOON-ENGLISH DANS LE NORD-OUEST DE L'ONTARIO - DIVERSES MESURES DE DEPOLLUTION

RESUME DU RAPPORT TECHNIQUE

Rédigé par

Le Comité directeur Canada-Ontario
1983

De: Comité directeur-Etude sur la pollution par le mercure dans le bassin Wabigoon-English

A : l'honorable Charles Caccia, C.P., député
Ministre de l'Environnement
Ottawa

l'honorable Andrew S. Brandt, député
Ministre de l'Environnement de l'Ontario
Toronto

L'honorable Alan W. Pope, député
Ministre des Richesses naturelles de l'Ontario
Toronto

Messieurs,

Le Comité directeur-Etude Canada-Ontario sur la pollution par le mercure dans le bassin Wabigoon-English est heureux de vous présenter ici son rapport final sur la pollution par le mercure dans le bassin hydrographique Wabigoon-English dans le nord-ouest de l'Ontario et de proposer diverses mesures pour lutter contre cette pollution. Le rapport comprend deux volumes. Le volume 1 est un résumé des grands problèmes, des conclusions de la recherche et des études de contrôle et des recommandations du Comité directeur. Le volume 2 est le rapport technique proprement dit et englobe tous les détails de chacune des études effectuées en vertu de l'accord Canada-Ontario en ce qui a trait à la pollution par le mercure dans le bassin hydrographique Wabigoon-English.

Présenté en février 1984.

CANADA

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Co-président

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M. D. Jeffs
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Dr. T. Brydges

M. K. Shikaze

Douglas P. Dodge
Dr. D. Dodge

AVANT-PROPOS

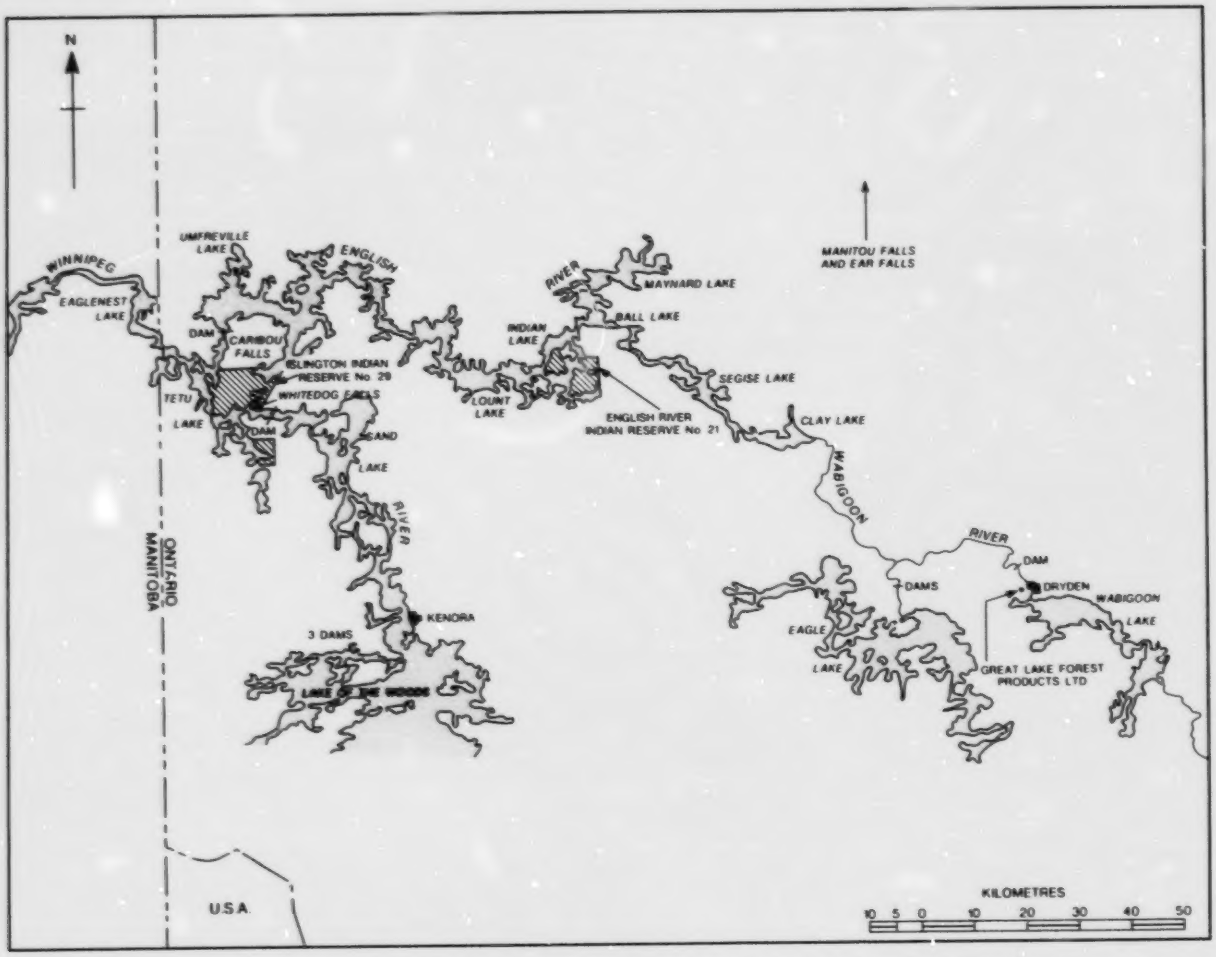
Ce rapport a été rédigé par le Comité directeur Canada-Ontario; ce Comité regroupe trois employés du gouvernement fédéral et trois autres du gouvernement provincial, chargés d'étudier les problèmes de pollution par le mercure dans le bassin hydrographique Wabigoon-English dans le nord-ouest de l'Ontario. Le rapport fait état des problèmes posés par l'évaluation de la pollution par le mercure dans le bassin et des méthodes susceptibles d'accélérer le processus de récupération naturel, et présente les conclusions et les recommandations du Comité. La matière du présent rapport a été tirée en grande partie du rapport technique qui l'accompagne; ce dernier est une compilation détaillée des résultats des recherches effectuées sur le terrain par les chercheurs. Certains chapitres du rapport technique ont déjà été publiés dans des journaux scientifiques. Bien qu'elles soient tirées d'une revue du rapport technique, les conclusions et les recommandations n'en sont pas moins celles du Comité directeur; elles ne sont cependant par nécessairement issues d'un consensus parmi les auteurs du rapport technique.

REMERCIEMENTS

Le Comité directeur désire remercier deux personnes dont l'aide a été très précieuse pour cette étude, mais dont les noms n'apparaissent ni dans le résumé, ni dans le rapport technique proprement dit.

La première personne, le D^r A.L. Hamilton, membre de la Commission mixte internationale à Ottawa, a été l'un des premiers à attirer l'attention du gouvernement sur les problèmes de pollution par le mercure dans la rivière Wabigoon. Il a suivi le déroulement de l'étude jusqu'à la fin, a fait au Comité directeur des commentaires judicieux sur le rapport technique et a aidé à arbitrer les divergences d'interprétation entre les équipes scientifiques.

La deuxième personne, M. W.A. Creighton, a joué un rôle important dans la gestion de l'étude au niveau provincial. Monsieur Creighton a participé activement à toutes les réunions du Comité directeur et son apport a été des plus précieux lors de la rédaction du rapport technique final.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WHITEDOG FALLS
TETU LAKE
DAM
SAND LAKE
RIVER
ONTARIO
MANITOBA
KENORA
3 DAMS
LAKE OF THE WOODS
U.S.A.
INDIAN LAKE
LOUNT LAKE
MAYNARD LAKE
BALL LAKE
ENGLISH RIVER INDIAN RESERVE No 21
SEGISE LAKE
CLAY LAKE
MANITOU FALLS AND EAR FALLS
WABIGOON
RIVER
DAM
DAMS
DRYDEN
WABIGOON LAKE
EAGLE LAKE
GREAT LAKE FOREST PRODUCTS LTD
KILOMETRES
10 5 0 10 20 30 40 50

FIGURE 1 CARTE DU BASSIN HYDROGRAPHIQUE ENGLISH-WABIGOON

INTRODUCTION

Le bassin hydrographique Wabigoon-English, situé dans le nord-ouest de l'Ontario et dans l'est du Manitoba, est l'un des bassins les plus gravement pollués par le mercure au monde (Armstrong et Hamilton, 1973). Deux communautés Ojibway, celle de Grassy Narrows et celle de White Dog, vivent sur les rives de la rivière English, respectivement en aval du lac Ball et au confluent de la rivière Winnipeg. Les membres de ces bandes pêchaient autrefois dans les eaux du bassin hydrographique tant à des fins commerciales que pour compléter leur approvisionnement alimentaire. Ils étaient également engagés comme guides pour les pêcheurs sportifs, pour la plupart venant des Etats-Unis. Comme l'économie de la région dépend surtout de l'industrie des pâtes et papiers et du tourisme, orienté principalement vers la pêche sportive, il y a conflit entre les utilisations des eaux. Ce rapport porte surtout sur la pollution par le mercure du bassin hydrographique et sur l'évaluation des méthodes qui pourraient être utilisées pour accélérer la récupération naturelle. Nous donnons ci-dessous une brève description du bassin hydrographique, ainsi qu'un aperçu historique des problèmes de pollution et des conséquences qu'ils ont sur les communautés autochtones.

Dans le nord-ouest de l'Ontario (figure 1), la rivière Wabigoon quitte le lac Wabigoon pour passer dans la ville de Dryden. Elle s'élargit environ 53 milles plus en aval pour former le lac Clay et pénétrer ensuite dans le lac Ball où elle rejoint la rivière English. Celle-ci s'écoule à travers une chaîne de lacs pour finalement se fondre dans la rivière Winnipeg qui se jette dans le bassin méridional du lac Winnipeg, à plus de 160 kilomètres à l'ouest de Dryden. Ce vaste bassin hydrographique, très peu peuplé, consiste en forêts boréales de relief bas, le terrain consiste en plaques d'argile et de till sableux reposant sur des ceintures précambriennes de granite et de roche verte.

La principale source de pollution dans le bassin est l'usine de papier exploitée par la Division de Dryden de la Great Lakes Forest Products Company (qui appartenait auparavant à Reed Ltd.). Cette usine de papier déverse ses déchets organiques dans la rivière Wabigoon depuis sa construction en 1913 (German, 1969). Certaines sections du lit de la rivière entre Dryden et le village de Quibell, près de l'entrée du lac Clay, sont par conséquent recouvertes de fragments de bois en putréfaction; on pouvait souvent observer des masses de mousse flottant sur la rivière et les débris en suspension dans les eaux étaient nombreux, mais à la suite d'un traitement primaire et secondaire des eaux résiduelles de l'usine, les conditions dans la rivière se sont grandement améliorées actuellement. L'usine d'épuration municipale de Dryden rejette également ses effluents dans la rivière, après un traitement primaire et secondaire.

Le problème de pollution par le mercure est surtout attribuable aux affluents d'une usine de chlore-alcali (Armstrong et Hamilton, 1973; Fimreite et Reynolds, 1972; Troyer, 1977) qui a été exploitée dans la région entre 1963 et 1975. Pendant cette période, des quantités illimitées de mercure, qui s'élèvent au total à environ 9 à 11 tonnes métriques, ont été déversées dans la rivière. En 1970, au moment où la Commission ontarienne sur les ressources en eau a pris conscience du problème, des mesures ont été prises et ces déversements de mercure ont été réduits d'environ 99 %. En 1975, l'usine de chlore-alcali a été convertie à un procédé ne faisant plus appel au mercure; toutefois, l'effluent du complexe industriel a continué à contenir de petites concentrations variables de mercure (5 à 10 kg par année). Le traitement primaire des eaux résiduelles de l'usine, commencé en septembre 1980, n'a pas été très efficace pour réduire les traces de mercure contenues dans l'effluent (extraction d'environ 20 %). Le traitement secondaire, qui a commencé en 1983, pourrait améliorer le taux d'élimination.

Armstrong et Hamilton (1973), Parks (1976) et Jackson (1979) ont établi la distribution du mercure dans les sédiments et le biote du bassin. La pollution se manifeste par de fortes concentrations de mercure chez les poissons dans tout le bassin, de Dryden jusqu'à la frontière du Manitoba, en aval. Les teneurs en mercure dépassent de beaucoup 0.5 partie par million (ppm) (Kenney, 1971; Scott et Armstrong, 1972; Armstrong et Hamilton, 1973; Fimreite et Reynolds, 1973; Annett et al., 1975; Bishop et Neary, 1976), limite fixée par la Direction générale des aliments et drogues du Canada pour le poisson de consommation mis en marché au Canada. Les teneurs moyennes en mercure relevées dans les brochets étaient constamment supérieures à 2.0 ppm, partout entre le lac Clay (le premier lac en aval de Dryden) jusqu'au lac Tetu, au confluent des rivières English et Winnipeg. Les teneurs en mercure des brochets de divers lacs de la région ne faisant pas partie du bassin Wabigoon-English variaient entre moins de 0.5 et 2.0 ppm (Bishop et Neary, 1976). D'autres organismes aquatiques tels que les écrevisses ont également été touchés par la pollution (Armstrong et Hamilton, 1973; Vermeer et al., 1973; Annett et al., 1975). Peu de temps après que les déversements de mercure ont été réduits, les teneurs en mercure du biote ont chuté rapidement (Armstrong et Scott, 1979); le rythme de cette diminution a cependant ralenti par la suite et les teneurs observées dans les poissons demeurent encore bien au-dessus des teneurs recommandées pour la consommation humaine sans restrictions.

La pêche commerciale a été interdite en 1971, mais la pêche sportive est demeurée permise. Le gouvernement de l'Ontario renseigne le public sur les teneurs en mercure du poisson et fait des recommandations sur la consommation des poissons contaminés dans son Guide to Eating Ontario Sport Fish - Northern Ontario, brochure mise à jour chaque année par le ministère de l'Environnement et le ministère des Ressources naturelles.

La pollution par le mercure a eu de graves effets directs et indirects sur les populations autochtones de la région, notamment sur les Ojibway des bandes de Grassy Narrows et de White Dog. Les

Ojibway engagés comme guides par les propriétaires de camp de pêche ont été fortement exposés au mercure; certains pourraient même souffrir d'un empoisonnement chronique du fait qu'ils avaient coutume de se joindre à leurs clients et de consommer avec eux les poissons fraîchement pêchés.

Depuis que le danger d'empoisonnement est devenu évident, les membres de la bande ont été avertis expressément de cesser de manger le poisson contaminé et le gouvernement de l'Ontario a commencé à approvisionner les collectivités en poissons congelés non contaminés.

Des enquêtes médicales effectuées entre 1971 et 1978 (Santé et Bien-être social Canada, 1973; Clarkson, 1976; Wheatley, 1979) ont relevé, chez certaines personnes dans les deux bandes, des teneurs en mercure dans le sang dépassant 100 parties par milliard (ppb) et cela même en hiver, lorsque ces teneurs devraient être à leur plus bas du fait de la consommation réduite de poisson. A des teneurs dépassant 100 ppb, un adulte humain est considéré en danger (Wheatley _et al_., 1979). Les teneurs élevées étaient de l'ordre de 100 à 500 ppb. La valeur maximale observée était de 600 ppb.

Les symptômes de l'empoisonnement au méthylmercure (la maladie de Minamata) peuvent être détectés d'abord parmi les 5 % d'adultes les plus vulnérables, dont le sang affiche des teneurs de l'ordre de 200 à 500 ppb. Les foetus sont toutefois encore plus sensibles que les adultes (Wheatley, 1979; Wheatley _et al_., 1979). Sur les 40 personnes à risque du nord-ouest de l'Ontario qui ont été soumises à des examens cliniques, aucune n'a montré de symptômes non équivoques d'empoisonnement par le mercure au 31 décembre 1978, bien que 10 d'entre elles présentaient des anomalies neurologiques qui pourraient y être attribuables. L'incertitude quant à la cause de ces anomalies vient du fait que les symptômes des formes douces de la maladie de Minamata ressemblent à ceux d'autres maladies, ce qui rend difficile l'établissement d'un diagnostic sûr (Wheatley, 1979; Wheatley _et al_., 1979).

Bien que la communauté scientifique ait recueilli beaucoup d'information au sujet de la pollution par le mercure dans le bassin Wabigoon-English, il s'est révélé impossible d'évaluer précisément le taux de récupération du bassin. Pour faire face à ce problème de pollution par le mercure et à ses effets prolongés sur la pêche commerciale, la pêche sportive et le tourisme dans les rivières Wabigoon et English, un accord a été signé entre les gouvernements fédéral et de l'Ontario; cet accord prévoyait le subventionnement conjoint, en vertu de la _Loi sur les eaux du Canada_, d'une étude de 300 000 $ destinée à mieux comprendre la situation. L'origine, le cheminement et l'évolution du mercure total et du méthylmercure ont ainsi été déterminés. On espérait, en comprenant mieux les mécanismes par lesquels le mercure pénètre dans le poisson, arriver à trouver des mesures correctives pour réduire la contamination et accélérer le processus de récupération du bassin hydrographique. Les objectifs précis de l'accord étaient les suivants : <<*réaliser des projets, à frais partagés ou non, en vue d'évaluer l'efficacité des diverses mesures de dépollution dans le bassin hydrographique Wabigoon-English; parmi ces projets, mentionnons les suivants:*

(1) une révision de toutes les teneurs en mercure des sédiments, de l'eau et du biote en vue d'établir l'exactitude des informations existantes, puis, selon les résultats obtenus, une enquête sur le cheminement, le transport et les taux d'accumulation et de distribution du mercure dans le bassin hydrographique Wabigoon-English; et

(2) une révision de toutes les données disponibles afin de déterminer les facteurs qui influent sur la disponibilité du mercure absorbable par le biote, et, selon les résultats obtenus, des expériences visant à établir l'efficacité des diverses façons de réduire cette disponibilité du mercure dans le bassin hydrographique Wabigoon-English.>>

CONCLUSIONS

Les grandes conclusions qui suivent sont, pour une large part, tirées du rapport technique complet. Les conclusions de nature générale sont en caractères gras et sont suivies des conclusions plus détaillées qui en découlent.

Les conclusions détaillées proviennent de l'analyse des données recueillies dans les bassins hydrographiques, dans des enclos d'essai, ainsi qu'en laboratoire.

I. **L'état du bassin des rivières Wabigoon-English s'améliore peu à peu, mais, sans une intervention directe, les teneurs en mercure observées dans les poissons demeureront trop élevées pendant encore de nombreuses années. La diminution des teneurs en mercure des poissons que l'on pourrait obtenir grâce à la mise en place de mesures correctives n'a pu être déterminée à partir des résultats de l'étude; ces mesures auraient cependant, par leur nature même, l'effet d'accélérer le taux de récupération du bassin. A mesure que l'on s'éloigne en aval de Dryden, les concentrations de mercure du biote baissent moins rapidement que les concentrations de mercure dans les sédiments. Cela semble lié à la disponibilité biologique accrue du mercure à mesure qu'on s'éloigne en aval de Dryden.**

i) Dans la plupart du biote du bassin, on a observé une baisse rapide et importante des concentrations de mercure entre le début des années 70 et des années 80 (figures 2, 3 et 4). Depuis les dix années que les effluents de mercure sont traités et surveillés, le bassin est revenu plus rapidement à ses conditions naturelles que ce que l'on prévoyait au milieu des années 70.

ii) Il y a eu diminution des concentrations de mercure dans les écrevisses depuis 1970, mais cette diminution a eu lieu en grande partie entre 1970 et 1973; les concentrations baissent maintenant à un rythme plus lent (figure 2).

iii) Les concentrations de mercure observées chez le brochet adulte (figure 3) et chez le doré (figure 4) ont décru depuis les années 70 et cette baisse devrait se poursuivre, mais à un rythme plus lent.

iv) Selon les prévisions, lorsque les poissons les plus vieux et les plus contaminés mourront au cours des prochaines années, les teneurs moyennes en mercure, calculées pour la population de dorés, baisseront davantage et seront plus représentatives du taux actuel

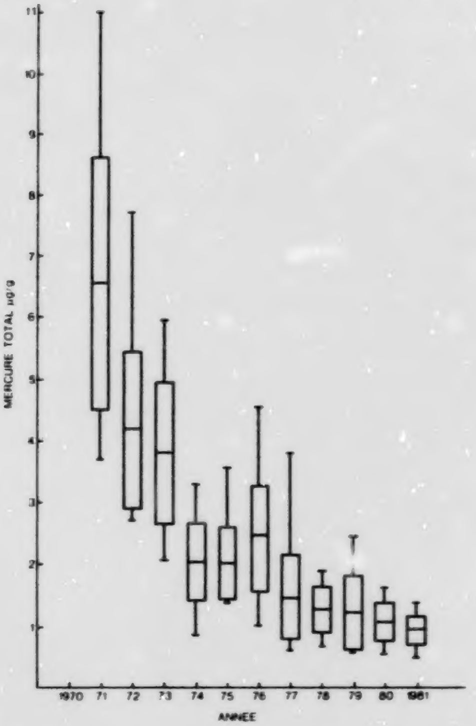

FIGURE 2 MOYENNE ECART-TYPE ET GAMME DES CONCENTRATIONS DE MERCURE DANS LE MUSCLE ABDOMINAL DES ECREVISSES DE PLUS DE 65 mm DE LONGUEUR TOTALE - LAC CLAY 1970-1981 (G.P. McRAE, FRESHWATER INST WPG.)

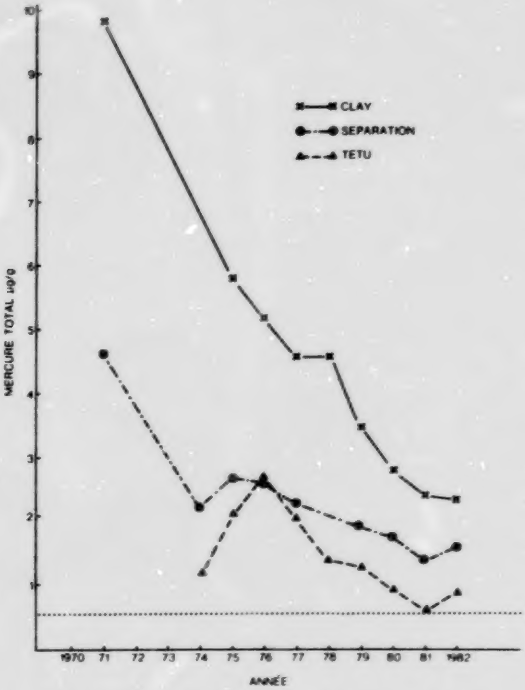

FIGURE 3 CONCENTRATIONS DE MERCURE DANS DES BROCHETS DE 60 cm PROVENANT DE TROIS LACS DU BASSIN HYDROGRAPHIQUE DE WABIGOON/ENGLISH/WINNIPEG. 1971-1982 (D'APRÈS BISHOP ET NEARY 1976) LA LIGNE POINTILLÉE REPRÉSENTE LA MOYENNE DE QUATRE SITES-TÉMOINS DU BASSIN

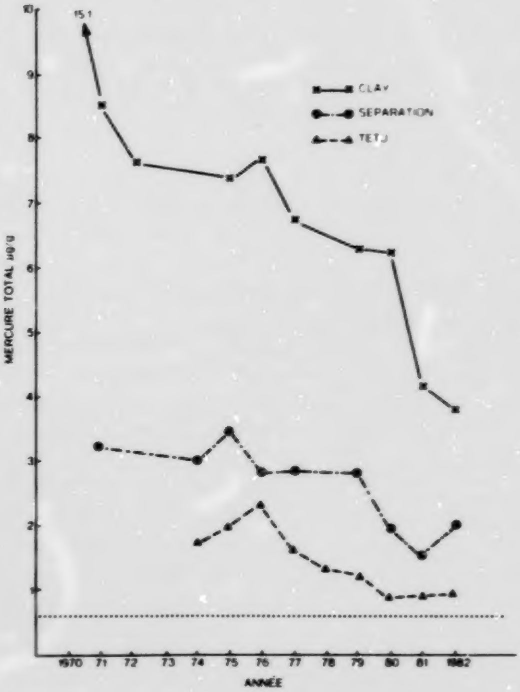

FIGURE 4 CONCENTRATIONS DE MERCURE DANS DES DORÉS DE 50 cm PROVENANT DE TROIS LACS DU BASSIN HYDROGRAPHIQUE WABIGOON/ENGLISH/WINNIPEG 1970-1982 LA LIGNE POINTILLÉE REPRÉSENTE LA MOYENNE DE QUATRE LACS-TÉMOINS

de pollution dans le bassin. Il y a un écart entre les concentrations observées dans les sédiments de surface et les concentrations relevées dans les plus vieux poissons qui peuvent avoir accumulé leur mercure il y a plusieurs années.

v) Au cours des deux dernières années, les trois grandes espèces de poisson de pêche sportive - brochet (figure 3), doré (figure 4) et corégone - ont accusé des baisses suffisantes de leur teneur en mercure pour permettre d'assouplir les avis de consommation restreinte. C'est dans le lac Tetu, dans le secteur occidental du bassin, que les améliorations sont les plus importantes en termes d'espèce et de taille pour les poissons qui peuvent être consommés avec ou sans restrictions. En fait, si on compare les données sur le poisson recueillies dans d'autres plans d'eau de régions avoisinantes non perturbées par les rejets industriels, on observe que les concentrations de mercure relevées dans le lac Tetu s'approchent des concentrations de fond. A mesure que l'on s'approche de Dryden par les lacs Separation et Ball, les avertissements de consommation restreinte deviennent très sévères, mais encore une fois, la situation a tendance à s'améliorer.

vi) Les concentrations de mercure dans les poissons du lac Clay, premier lac en aval de Dryden, sont si élevées que la plupart des poissons de pêche sportive sont impropres à la consommation humaine. Toutefois, même dans ce plan d'eau, les concentrations de mercure dans les poissons ont diminué (figures 3 et 4).

vii) La méthylation du mercure dans le bassin est provoquée en grande partie par des processus microbiologiques.

viii) Pour la première fois, la méthylation du mercure dans la colonne d'eau et les intestins des poissons a été analysée. Dans les poissons, elle est proportionnelle à la teneur en mucus de l'intestin. Il y a donc deux autres sources de méthylmercure en plus de celles des sédiments de fond déjà connues.

ix) Les concentrations de mercure du biote sont reliées aux concentrations de mercure total (mercure sous toutes ses formes) et de méthylmercure (mercure combiné à des groupes méthyle organiques et considéré comme une forme plus toxique) dans la colonne d'eau.

II. **Des mesures visant à augmenter, dans la colonne d'eau, la charge en sédiments lacustres propres pourraient accélérer la vitesse de sédimentation et, en retour, diminuer les concentrations de mercure à l'interface sédiments-eau. En plus de réduire l'émission de mercure des sédiments de fond, cette charge accrue en matières en suspension dans la colonne d'eau permettrait de réduire la disponibilité biologique du mercure. Cela pourrait être réalisé en draguant le fond et en remettant en suspension, des sédiments lacustres non contaminés et riches en argile.**

1) En enclos, les sédiments argileux ont permis de réduire de dix fois la teneur en mercure du biote (figure 5), tandis que le sélénium n'a permis de la réduire que de moitié ou même pas du tout lorsque la production primaire s'accroît. Les sédiments lacustres riches en argile remis en suspension dans les enclos permettent de lier le mercure beaucoup mieux que ne le fait l'argile des rivages des cours d'eau. Cela pourrait être dû aux matières organiques (probablement des matières organiques <<dissoutes>> de granulométrie inférieure à 0.45 μ) et aux oxydes de fer et de manganèse qui recouvrent les sédiments. Il reste bien sûr du mercure dans la colonne d'eau parce que le mercure s'associe aux particules de petite taille, mais il ne s'accumule pas biologiquement.

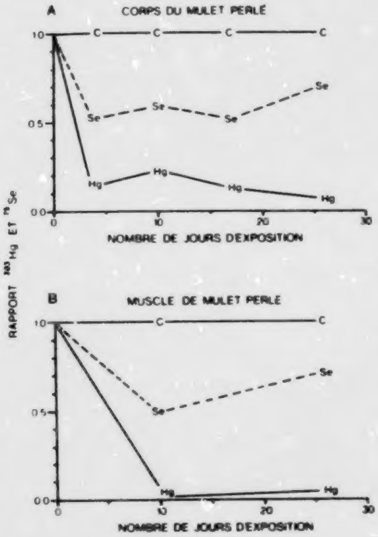

FIGURE 5 INHIBITION DU MERCURE 203 (Hg) ET BIOACCUMULATION DU SÉLÉNIUM 75 (Se) DANS TOUT LE CORPS (DIAGRAMME DU HAUT) ET DES ÉCHANTILLONS DE MUSCLES (DIAGRAMME DU BAS) DU MULET PERLÉ PAR ADDITION DE SÉDIMENTS INORGANIQUES RICHES DANS UN ENCLOS. LES DONNÉES SONT EXPRIMÉES SOUS FORME DE RAPPORTS D'ACTIVITÉS ^{203}Hg ET ^{75}Se DANS LES SÉDIMENTS EN SUSPENSION DIVISÉS PAR L'ACTIVITÉ DANS LES ENCLOS-TÉMOINS (C)

ii) Le mercure particulaire présent dans la colonne d'eau était à plus de 98 % inextractible au moyen d'une série de réactifs doux et n'est probablement pas facilement disponible biologiquement.

iii) Le mercure contenu dans le silt est plus facilement soluble et, par conséquent, méthylable que le mercure qui se trouve dans les copeaux de bois, qui sont plus abondants à proximité du complexe industriel de Dryden.

iv) L'augmentation de la teneur en matières en suspension à 18 mg/L dans une expérience en enclos n'a fait diminuer ni la production primaire, ni la croissance des poissons.

III. Le mercure contenu dans les sédiments de fond où que ce soit dans les lacs ou les rivières contribue à court terme (mois) au problème de pollution, mais, à long terme (années) les sources situées en amont prennent de l'importance. La partie du bassin située en aval de Dryden jusqu'à l'entrée du lac Ball demeure très contaminée, quelle que soit la norme choisie. De la sortie du lac Ball jusqu'à la frontière du Manitoba, le problème est cependant moins grave.

i) Les rejets industriels actuels ne semblent être une source importante de mercure ni dans le lac Clay, ni en aval.

ii) Les concentrations de méthylmercure dissous et les charges de méthylmercure totales ont augmenté en aval dans la rivière Wabigoon, de Dryden au lac Clay.

iii) Entre Dryden et le confluent de la rivière Eagle, les concentrations de mercure particulaire et de méthylmercure, de mercure soluble total et de mercure total atteignent leur niveau maximal pendant les crues printanières à cause de la remise en suspension des sédiments de fond contaminés et de leur charriage en aval.

iv) Entre Dryden et le lac Clay, les concentrations de méthylmercure soluble sont faibles au printemps et élevées en été.

v) Les concentrations de mercure dans l'eau sont davantage fonction des sédiments de surface que des sédiments de fond.

IV. Les concentrations de mercure et de ses différentes formes chimiques et physiques dans la colonne d'eau sont influencées par plusieurs variables, notamment la température, l'oxygène, la teneur en matières en suspension et l'activité microbienne. En tout lieu donné, la répartition du mercure entre les sédiments de surface, l'eau et les matières en suspension se stabilisent de façon caractéristique en quelques jours. Toutefois, il y a probablement des pertes de la surface de l'eau vers l'atmosphère, pertes qui n'ont pas été mesurées pendant les enquêtes. Dans ce bassin contaminé, la principale source influant sur le mercure contenu dans la colonne d'eau est la concentration de mercure des sédiments de surface. La forme du mercure influe sur sa disponibilité biologique.

i) Les sédiments sont actuellement la principale source de mercure dans l'eau, du moins entre Dryden et la sortie du lac Ball.

ii) La température influe sur la concentration de mercure dans l'eau en un lieu et à un moment donnés (figure 6).

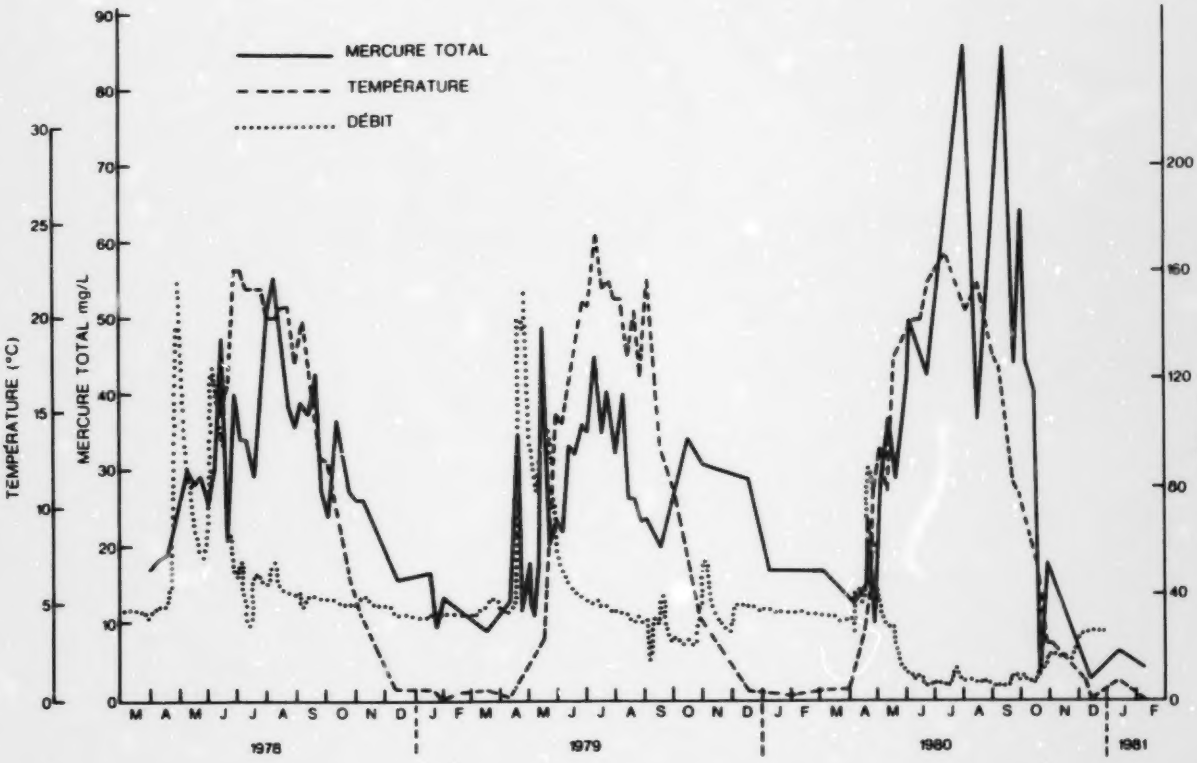

FIGURE 6 DONNÉES SUR LE MERCURE TOTAL ET LA TEMPÉRATURE, EAU D'ENTRÉE DANS LE LAC CLAY, DÉBIT À QUIBELL MARS 1978 À FÉVRIER 1981

iii) L'eau atteint sa concentration maximale de mercure pour une température donnée en quelques jours. Les sédiments continuent probablement à libérer du mercure par la suite du fait de l'activité microbienne, mais la concentration des eaux ne change pas; il semble donc que du mercure s'échappe dans l'atmosphère.

iv) En été, lorsque la température des eaux est élevée et qu'aucune particule n'est remise en suspension, le méthylmercure dissous est fonction du mercure dissous total dans l'eau. Au printemps, lorsque les sédiments sont remis en suspension, le méthylmercure dissous et en suspension n'est pas fonction des concentrations de mercure total.

v) Le rapport méthylmercure-mercure total dans les sédiments de surface augmente à mesure que l'on s'éloigne de Dryden. Le rapport méthylmercure-mercure total dans l'eau augmente également en allant vers l'aval, mais les concentrations moyennes de méthylmercure et de mercure total décroissent généralement, sauf dans le lac Clay, où la concentration de méthylmercure augmente.

vi) La concentration de méthylmercure dans l'eau est fonction variable de la concentration de mercure total, le rapport de l'une à l'autre changeant en allant vers l'aval du bassin (figure 7).

vii) Le méthylmercure et le mercure sont liés aux sédiments de différentes façons. Le méthylmercure est associé au soufre ainsi qu'aux oxydes de fer. Le mercure est associé aux matériaux de fer humide ainsi qu'au fer et au manganèse facilement extractibles.

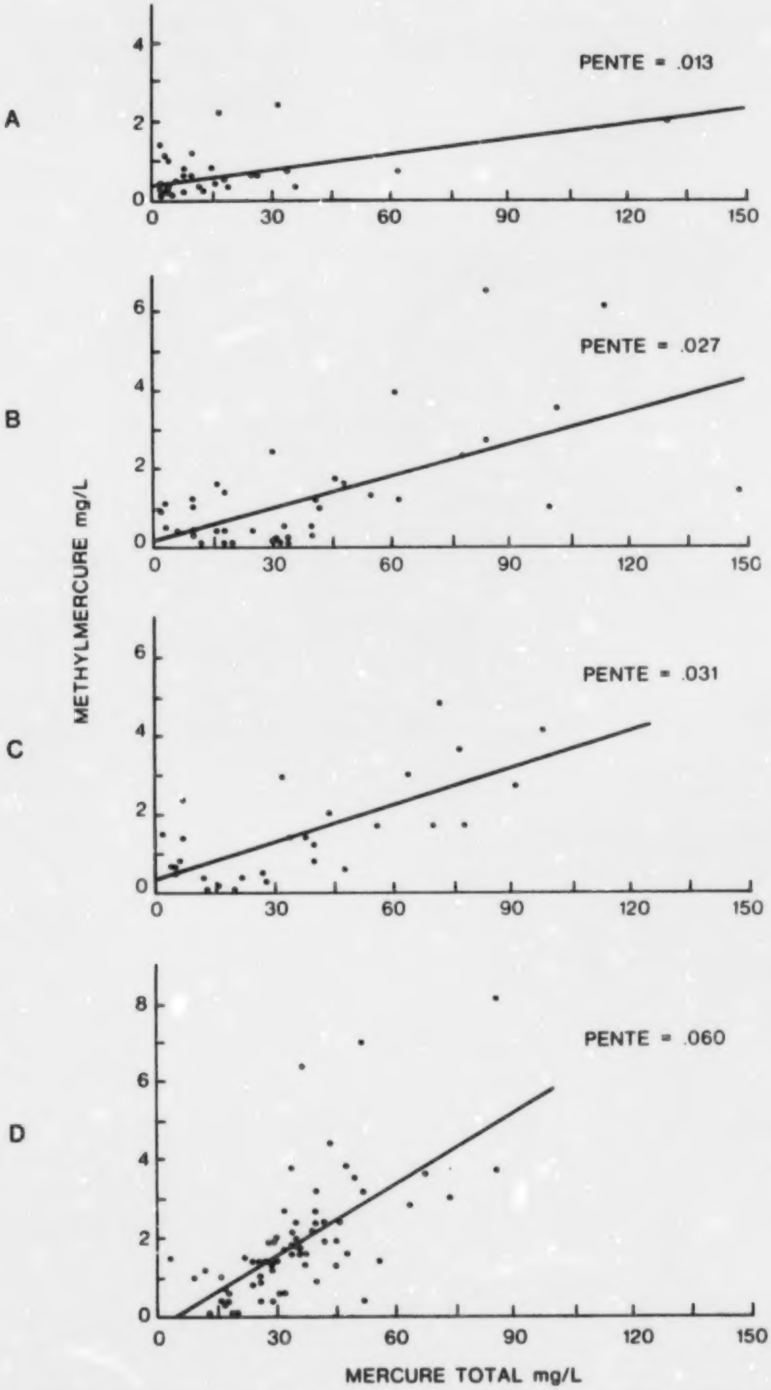

FIGURE 7 RAPPORT ENTRE LE MÉTHYLMERCURE ET LE MERCURE TOTAL PENDANT LES PÉRIODES OÙ LE DÉBIT N'EST PAS À SON PLUS HAUT, LAC WABIGOON-LAC CLAY, 1978-1980. (EMPLACEMENT (A) LAC WABIGOON; (B) ENTRÉE DU BARRAGE WAINWRIGHT; (C) MINNITAKI; (D) ENTRÉE DU LAC CLAY.)

V. Un certain nombre d'autres mesures d'amélioration ont été examinées dans le cadre de cette étude. On a envisagé l'emploi de sélénium pour atténuer les effets de la pollution par le mercure. Il ressort en effet de la documentation que le mercure est moins toxique pour les consommateurs de poisson lorsqu'il est associé au sélénium. Les expériences effectuées visaient à déterminer si les poissons absorbaient le sélénium associé au mercure. Bien que cette addition de sélénium semble efficace, il faudra poursuivre les recherches avant d'envisager sérieusement sa mise en application. Parmi les autres méthodes qui se sont révélées moins appropriées, mentionnons les suivantes: l'addition de sulfate en vue d'immobiliser le mercure dans les sédiments sous forme de sulfure mercurique insoluble et l'addition de matériaux algaux en vue de favoriser la croissance des poissons et, par là, de réduire les concentrations de mercure dans les poissons par dilution. Le labourage des sédiments de surface en vue de réduire les concentrations de mercure n'a pas été tenté à cause des difficultés techniques prévues.

i) Le rapport mercure-sélénium dans le poisson est élevé du fait des fortes concentrations de mercure, mais également à cause des concentrations anormalement faibles de sélénium dans le bassin.

ii) Une concentration de 100 ppb de sélénium dans l'eau a permis de réduire de 50 % l'absorption de mercure par les poissons (figure 8). Cet effet se transmet par la chaîne alimentaire plutôt que par l'eau.

iii) On peut donc s'attendre à une réduction des concentrations de mercure dans les poissons de pêche sportive si l'on augmente la concentration de sélénium dans l'eau. Une certaine réduction peut également se produire même à une concentration de sélénium aussi faible que 1 ppb (figure 8).

iv) D'après les tests de toxicité et une revue de littérature, il semble que la concentration sûre de sélénium soit faible. La norme canadienne sur la teneur en sélénium des eaux potables est de 10 ppb.

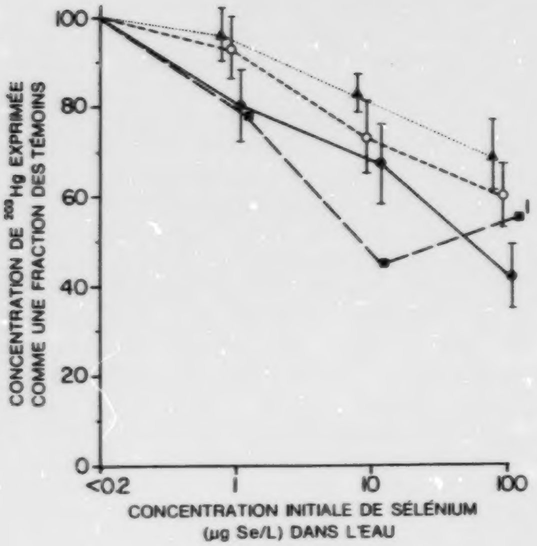

FIGURE 8 ACCUMULATION DE MERCURE-203 DANS TOUT LE CORPS DE L'ÉCREVISSE ADULTE (○), DU MULET PERLE (▲), DE LA JEUNE PERCHAUDE D'UN AN (●), ET DU MEUNIER NOIR JUVÉNILE (■) DANS LES ENCLOS. LES DONNÉES SONT EXPRIMÉES COMME DES PROPORTIONS DANS LESQUELLES LES ACTIVITES DU ^{203}Hg CHEZ LES ANIMAUX EXPOSES AU Se SONT DIVISÉES PAR LES ACTIVITÉS MOYENNES DES TÉMOINS COMBINÉS. LES MOYENNES (±Se) DE PLUSIEURS PÉRIODES D'ÉCHANTILLONNAGE (ÉCREVISSE: 4, MULET: 6, PERCHAUDE: 4, ET MEUNIER: 1) SONT PRÉSENTÉES POUR CHAQUE ORGANISME. UN SEUL MEUNIER FUT RETIRÉ DE L'ENCLOS CONTENANT 100 µg Se/L (EXPOSANT 1)

RECOMMANDATIONS

Les recommandations qui suivent sont présentées par ordre de priorité. Nous nous sommes limités aux recommandations applicables en vertu des conclusions présentées ci-dessus. Ces conclusions se fondent sur le rapport technique; celui-ci contient par ailleurs de nombreuses autres conclusions, moins essentielles mais non moins importantes. Nos recommandations ne portent que sur les mesures correctrices jugées techniquement réalisables. Nous croyons qu'elles permettront d'accélérer le processus de récupération du bassin, mais, la mesure dans laquelle les concentrations de mercure dans le poisson seront diminuées n'a cependant pu être déterminée quantitativement.

Il est clair que, même si c'est la pollution qui est la maladie, ce sont d'abord les symptômes qui affectent les populations autochtones, les pêcheurs locaux, les pêcheurs sportifs et les propriétaires de chalets de pêche.

Nous sommes conscients que l'allocation de fonds à des fins d'amélioration peut, dans un contexte plus large, ne pas être la meilleure réponse au problème. En particulier, il est évident que le système continue à récupérer de lui-même naturellement.

Les recommandations du Comité sont les suivantes:

I. POURSUITE DU PROGRAMME DE SURVEILLANCE DU MERCURE ET DE DIRECTIVES PORTANT SUR LA CONSOMMATION DU POISSON

Les échantillonnages et les analyses annuelles des poissons prélevés dans les quatre plans d'eau régulièrement testés (les lacs Clay, Ball, Separation et Tetu) doivent se poursuivre. Des analyses des poissons de pêche sportive dans tous les autres lacs où l'on a déjà effectué des tests dans le bassin Wabigoon-English devraient être effectuées au cours des deux prochaines années pour mettre à jour tous les guides de consommation et évaluer les tendances de la pollution par le mercure dans les autres parties du bassin.

II. TENUE D'UN PROJET-PILOTE SUR LA REMISE EN SUSPENSION SEMI-CONTINUE DE SEDIMENTS NON CONTAMINES PAR LE MERCURE DANS LES ENDROITS CRITIQUES DU BASSIN

D'après les conclusions de l'étude, la remise en suspension de sédiments lacustres serait une méthode prometteuse pour remettre en état le bassin hydrographique Wabigoon-English. Il y a toutefois un certain nombre de facteurs qui peuvent influer sur le succès de cette méthode dans un bassin hydrographique aussi complexe que celui des rivières Wabigoon-English.

Un projet-pilote de remise en suspension semi-continue des sédiments pourrait comporter les éléments suivants:

a) Injection de sédiments de fond du lac Wabigoon dans la rivière du même nom;

b) Injection de sédiments de fond de l'est du lac Clay dans l'ouest du lac du même nom et en aval;

c) Injection de sédiments de fond provenant du secteur nord du lac Ball dans le bassin de la rivière English.

Compte tenu des trois emplacements choisis, nous croyons que c'est l'option (b) qui offre le plus de possibilités tant pour contrôler les changements dans la concentration de mercure des poissons que pour prouver que la méthode est une réussite. La remise en suspension devrait être efficace à court terme en réduisant la disponibilité biologique du mercure dans la colonne d'eau et, à long terme, en réduisant les concentrations de mercure dans les sédiments de surface.

Si l'expérience réussit à l'emplacement (b), nous recommandons qu'elle soit reprise au site (c), puis au site (a).

Nous tenons à souligner que les sédiments non pollués par le mercure qui sont remis en suspension doivent provenir du lit et non des rivages de la rivière ou du lac; les sédiments provenant des rivages sont en effet inefficaces.

Nous avons supposé que le volume de sédiments remis en suspension serait suffisant pour réduire la disponibilité biologique du mercure dans la colonne d'eau et diminuer de façon efficace les concentrations de mercure des sédiments de surface.

Ce projet-pilote devrait permettre à la fois d'évaluer la faisabilité technique de la méthode et d'en estimer les coûts d'application.

III. EXTRACTION DES SEDIMENTS PAR DRAGAGE ENTRE DRYDEN ET LE LAC CLAY

Les sédiments de la rivière Wabigoon, entre le lac Wabigoon et le lac Clay, contiennent une quantité importante de mercure et continueront à être une importante source de mercure dans le bassin.

Les teneurs en mercure de la colonne d'eau sont fonction des teneurs en mercure des sédiments de fond dans chaque section particulière de la rivière. Par conséquent, tout plan de dragage et d'élimination hors rivière des sédiments contaminés doit débuter en amont, à partir de Dryden en descendant vers le lac Clay. L'enfouissement des sédiments dans cette section de la rivière est impossible à long terme; les nouveaux sédiments

seraient en effet érodés et les sédiments contaminés exposés de nouveau. Il est jugé inutile de procéder à des opérations de dragage en aval du lac Clay.

Le coût de l'extraction des sédiments contaminés entre Dryden et le lac Clay et du confinement des sédiments contaminés dans des décharges appropriées, construites à terre près de la rivière Wabigoon, a été évalué à 19 millions de dollars (dollars de 1981). Il est possible d'obtenir une meilleure estimation des coûts du dragage et du confinement des sédiments contaminés en effectuant une enquête sur le terrain dans le but de mieux définir les données d'ingénierie (par exemple, une étude au sonar visant à établir le profil du lit de la rivière et à déterminer le nombre de billes de bois qui s'y trouvent, les conditions du sol à la décharge, etc.). Ces études devront être faites avant la prise de décision finale pour le dragage, décision qui devrait également tenir compte des résultats du projet de remise en suspension des sédiments.

Bien qu'il soit apparu que le réservoir Wainwright ne soit ni une source, ni un réservoir de mercure sur une base annuelle, ce réservoir n'en est pas moins une source de mercure pendant le ruissellement printanier; pour améliorer efficacement la situation en aval, les sédiments contaminés du réservoir Wainwright devraient être complètement ou partiellement dragués et le fond recouvert, par pompage, d'une couche de sédiments de fond propres.

IV. AUTRES ETUDES SCIENTIFIQUES

Par suite des études scientifiques effectuées à ce jour, deux secteurs de recherche prometteurs ont pu être déterminés:

(a) Perte de mercure dans l'atmosphère

D'après l'augmentation des concentrations de mercure dans les eaux observée en été, augmentation reliée à la température, il semble qu'une partie du mercure soit libérée dans l'atmosphère à cette époque de l'année. Des études devraient être effectuées pour quantifier cette perte.

(b) Autres tests d'efficacité sur le sélénium comme agent d'absorption du mercure

Bien qu'il n'ait pas été aussi efficace que les sédiments en suspension, le sélénium s'est révélé capable de réduire l'absorption du mercure par le biote. Les concentrations de sélénium sont également apparues anormalement faibles dans le bassin à cause des conditions géologiques naturelles. Pour arriver à réduire les concentrations de mercure dans le biote, les eaux doivent atteindre une teneur minimale en sélénium d'environ 1 ppb. Cette concentration est bien inférieure à la norme établie pour l'eau potable. L'élévation des concentrations de sélénium à ce niveau par addition de sel de sélénite dans la rivière serait de loin la méthode d'amélioration la moins coûteuse. Cependant, d'après les expériences toxicologiques effectuées sur divers éléments du biote en enclos d'essais et la revue de littérature portant sur la toxicité du sélénium, il semblerait imprudent d'adopter cette méthode sans effectuer auparavant des études plus poussées, notamment au niveau d'un lac entier.

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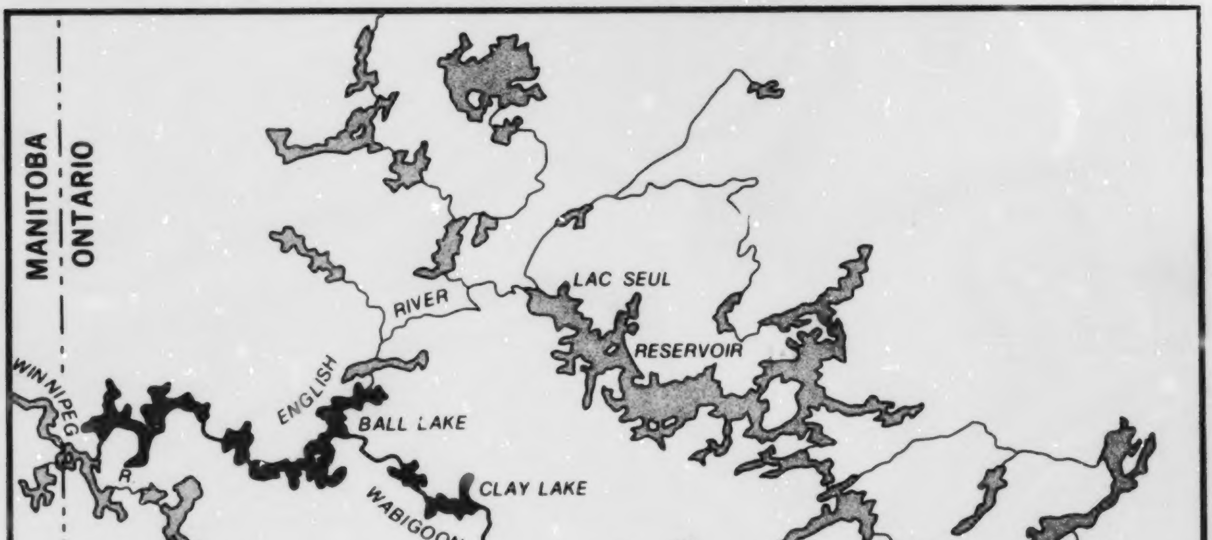
Mercury Pollution in the Wabigoon-English River System of Northwestern Ontario, and Possible Remedial Measures



MANITOBA
ONTARIO
LAC SEUL
RESERVOIR
RIVER
ENGLISH
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BALL LAKE
CLAY LAKE
WABIGOON
RIVER
Dryden
WABIGOON LAKE
CANADA
RAINY
RIVER
USA

Technical Report

Government of Canada

Government of Ontario

MERCURY POLLUTION IN THE WABIGOON-ENGLISH RIVER SYSTEM OF NORTHWESTERN ONTARIO, AND POSSIBLE REMEDIAL MEASURES

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Cat. No. Em 37-67/1984E

ISBN 0-662-13099-5

Preface

This Technical Report is the second of two volumes containing the results of investigations of mercury pollution in the Wabigoon-English River System of Northwestern Ontario conducted by scientists of the governments of Canada and Ontario during 1978, 1979 and the winter and spring of 1980. The report is a detailed compilation concerned with the assessment of mercury pollution in the system and with the evaluation of methods which might be employed to accelerate natural recovery of the system. Volume 1 is a Summary which highlights the Problem, the Conclusions of the research and monitoring studies, and the Recommendations agreed to by the Steering Committee which managed the joint federal-provincial study.

Préface

Ce rapport technique est le second de deux volumes contenant les résultats d'enquêtes sur la pollution par le mercure dans le bassin des rivières Wabigoon et English, dans le nord-ouest de l'Ontario, enquêtes qu'ont menées des scientifiques des gouvernements du Canada et de l'Ontario, durant les années 1978 et 1979 et au cours de l'hiver et du printemps 1980. Le rapport constitue une compilation détaillée touchant l'évaluation de la pollution par le mercure dans le système ainsi que l'évaluation des méthodes qui pourraient servir à accélérer le retour des eaux à leur état naturel. Le volume 1 résume les faits saillants du problème, les conclusions des études de recherche et de surveillance, de même que les recommandations adoptées par le comité directeur responsable de l'étude conjointe fédérale-provinciale.

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A

MERCURY CONTAMINATION of the WABIGOON/ENGLISH/WINNIPEG RIVER SYSTEM

Causes, Effects and Possible Remedial Measures

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ONTARIO MINISTRY OF THE ENVIRONMENT

ACKNOWLEDGEMENTS

We wish to acknowledge the guidance of the Steering Committee and technical advice generously provided by the following individuals: Dr. A. L. Hamilton, International Joint Commission; F. A. J. Armstrong, Freshwater Institute; Dr. A. S. W. de Frietas, National Research Council; Dr. R. J. Allan, Canada Centre for Inland Waters; Dr. T. Brydges and Mr. B. P. Neary, Ontario Ministry of the Environment; Drs. J. W. M. Rudd and T. A. Jackson and Mr. M. Turner, Freshwater Institute; Dr. D. R. Miller, National Research Council; Messrs. J. N. Bishop and N. Conroy, Ontario Ministry of the Environment.

Support for field studies was provided by Ms. P. Almost and Messrs. D. Romani, K. Marsh, C. Nanni, E. Hansen, L. Baxter and D. Pugh.

We are grateful to Messrs. A. Lutz and C. Tam, Dr. T. A. Jackson and Mr. R. Woychuk of the Freshwater Institute for total mercury and methylmercury analysis of water samples. For the chemical analysis of water samples, we are grateful to Mr. M. Stainton of the Freshwater Institute and to Mr. J. Taylor and co-workers at the Ministry of the Environment Laboratory in Thunder Bay.

We express thanks to the federal research team for their support, particularly at the beginning of our program, for jointly sampling Clay Lake and for supplying Clay Lake data collected prior to August, 1978. We are also grateful to the following individuals and organizations for data; Water Survey of Canada and Great Lakes Forest Products Limited for flow data; Mr. D. Draper, Ontario Ministry of the Environment and co-workers for time-of-travel studies; Dr. W. I. Heathcote, Ontario Ministry of the Environment for making a hydrological assessment; Mr. K. Suns and Ms. C. Currie, Ontario Ministry of the Environment and Mr. G. MacRae and Dr. D. P. Scott, Freshwater Institute for biological data. Mr. B. P. Neary kindly provided analysis of some of the biota data. The figures for the report were drafted by the Cartographic and Drafting Section, Ontario Ministry of the Environment.

We are grateful to our supervisor, Mr. W. A. Creighton, for his support and forebearance during the study and preparation of the report and to Dr. H. D. Griffin, Ontario Ministry of the Environment, for a major contribution to the editing of the final document.

SUMMARY

More than a decade after the cessation of substantial mercury discharges to the Wabigoon River at Dryden, mercury remains elevated in aquatic organisms (biota), sediments and waters of the Wabigoon/English/Winnipeg River system. The Wabigoon River system itself was the most severely contaminated: flesh from adult walleye in Clay Lake, the first lake downstream of Dryden, contained more than 3.5 μg/g of mercury. These levels were at least five times higher than levels in comparable fish in nearby uncontaminated waters and more than the limit of 0.5 μg/g established by the Canadian Food and Drug Directorate for unrestricted human consumption. Biota in the English/Winnipeg river system, while much lower in mercury than those in the Wabigoon River system, still contained 2 to 3 times the amount of mercury in biota from uncontaminated lakes. Although mercury in fish has declined sharply since 1970, the current rate of decline is slow. Young fish and crayfish were good biological indicators of mercury contamination.

Our data suggest that partitioning of inorganic and organic mercury between sediment, water and suspended particles occurs in a period of a few days and reaches a dynamic "steady-state". In the contaminated watercourse, mercury in sediments governs mercury levels throughout the ecosystem. At steady-state, concentrations of methylmercury in water depend more on environmental variables than on the rate of production. Temperature has a strong effect on both total and methylmercury concentrations in water; concentrations fluctuate seasonally. Total mercury and methylmercury levels in water at any site are controlled by exchange processes between water and local sediments and by mercury transported by the river from upstream. There were strong relationships between mercury concentrations in crayfish, pike and perch. Both biological and chemical data indicate that each sampling site can be considered a similar ecosystem at a different degree of contamination.

We ascribe contamination of biota in the Wabigoon/English River system primarily to past industrial loadings from a pulp and paper manufacturing complex in Dryden. Current industrial discharges are only about 0.5 percent of pre-1970 levels and have only a marginal impact on downstream biota. In the Winnipeg River system, industrial mercury source(s) at Kenora probably contributed to elevated mercury in fish and other biota downstream of the English/Winnipeg River confluence.

If no remedial measures are instituted, the prognosis for this system is not favourable. Data from crayfish and young sportfish indicate that much of the Wabigoon River system between Dryden and Ball Lake would remain severely contaminated for the foreseeable future. Mercury concentrations in adult sportfish in Clay Lake may not recover to normal levels for many decades. Biota in the English River system should return to normal levels earlier than biota in the Wabigoon river system.

Mercury levels in fish and other biota may be decreased by reducing mercury levels in active surface sediments or by reducing the bioavailability of mercury in the water. Mercury concentrations in surface sediment can be reduced either by dredging to remove contaminated material or by covering it with clean material. It may be possible to reduce the bioavailability of mercury by maintaining high suspended solids levels in the water through the suspension of clean clay.

It is clear that there are no quick, simple remedies to restore the Wabigoon and English River systems but the following measures are recommended for consideration by the Steering Committee in formulating its recommendations to the Canadian and Ontario governments.

1. Removal by dredging of contaminated sediments from the 62 km reach of the Wabigoon River between Dryden and the Highway 105 crossing, and confinement of these contaminated sediments in disposal areas close to the river.
2. The covering of contaminated sediments in Clay Lake with clean clay or sediment to reduce mercury feedback.
3. The semi-continuous addition of clean sediment to the water column at selected sites in the river system following field trials to confirm the economic and technical feasibility of the method.

It may be appropriate to use more than one of these techniques in a remedial program to restore or accelerate the recovery of the Wabigoon and English Rivers from the effects of mercury pollution.

1. INTRODUCTION

Concern for mercury discharges to the environment intensified in the 1950's, following mercury poisoning of people in Minamata, Japan, by the consumption of contaminated fish. Many facets of the biogeochemical cycling of mercury have been studied since that time. Jensen and Jernelov (1969) discovered that relatively innocuous inorganic forms of mercury could be transformed in the aquatic environment into methylmercury, a very potent neurotoxin.

The problem of excessive mercury concentrations in fish flesh has been linked to man's discharge of this element into aquatic systems. However, mercury is ubiquitus in nature, and most water bodies in Ontario contain some large fish with mercury concentrations greater than 0.5 µg/g (micrograms of mercury per gram of sample, oven dry weight) (Bishop and Neary, 1976), the criterion established by Health and Welfare Canada for unrestricted consumption. Occasionally, fish containing mercury above desirable limits are even found in waters not affected by industrial discharges. Although concern is for elevated levels of mercury in fish, methylmercury is of primary interest since it is much more toxic than inorganic mercury. In fact, metallic mercury has been safely given orally for medicinal purposes, because of the low toxicity of the inorganic form.

Early studies on waters downstream from a chlor-alkali plant and kraft pulp mill at Dryden, Ontario, indicated that fish from Clay Lake on the Wabigoon River system contained mercury concentrations of 10-20 µg/g, higher than levels reported for any other freshwater fish in the world (D'Itri, 1978). Subsequent investigations (Armstrong and Hamilton, 1973, Bishop and Neary, 1976; Parks, 1976) revealed that over 250 km (kilometres) of the Wabigoon/English/Winnipeg River system were adversely affected by the release, between 1962 and 1969, of an estimated 10 metric tons of mercury from the mercury cell chlor-alkali operation in Dryden. The total industrial complex is currently operated by the Dryden Mill Division of Great Lakes Forest Products Limited, but was previously owned by Reed Limited from 1970 to 1979, and was called Dryden Paper Limited before 1970. During the study period, there was no treatment of the total effluent from this source, other than a small holding pond designed to eliminate foam entering the river. Effluents have undergone primary treatment since November, 1980, and secondary treatment is expected to commence in 1983.

In 1970, abatement measures sharply curtailed mercury losses, and in October, 1975, the mercury cells were dismantled. Despite the 99 percent reduction in the amount of mercury lost from the mill complex, biota in contaminated waters continued to exhibit very high mercury concentrations.

To find methods to alleviate this long-term problem, a joint Federal/Provincial study was conducted over a 2-year period beginning in June, 1978. Federal studies investigated possible amelioration techniques in Clay Lake, while the Ontario Ministry of the Environment was charged with examining mercury concentrations in waters, sediments and biota. One of the main objectives of the study was to assess the significance of the Wabigoon River as a mercury source for Clay Lake biota, particularly fish, since certain lake restoration techniques pre-supposed a "clean" inflow.

It was desirable to have answers to the following questions before discussing amelioration options for the Wabigoon/English Rivers.

1. Why and how do fish accumulate methylmercury?
2. How and where is methylmercury produced?
3. What environmental factors affect methylmercury concentrations and bioavailability of the methylmercury to which biota are exposed?

Figure 1.1 is a simple model of how methylmercury is accumulated in predacious fish, and would be applicable to any other fresh-water ecosystem. Fish exposed to methylmercury in their food and surrounding waters have high mercury body burdens. Methylmercury forms extremely stable complexes with anionic sulphur ligands in living cells. It follows that the biota will retain methylmercury, a fact borne out by many investigations. Most of the mercury in fish is methylmercury, with predators at the top of the food chain (pike and pickerel) generally having over 85 percent of their total body burden in this form. The relative importance of methylmercury uptake from food or water is not known, but uptake from either source depends on species-specific factors such as feeding habits, metabolism, growth rates, and size. The bioavailability of methylmercury and the physical and chemical characteristics of the water are also important factors. It appears that methylmercury in water and fish diet is derived from sediments.

Methylmercury can be produced by a number of biotic or abiotic processes in the aquatic environment. Although methylmercury production studies in situ are few, the continued occurrence of elevated mercury levels in biota long after point sources have ceased suggests that the previously contaminated sediment was a continuing source of methylmercury. Laboratory studies also indicate that the pathways of methylmercury to fish are such that the mercury can originate in sediment.

The Wabigoon River system has a wide-range of physical and chemical characteristics. Thus, it may be more useful to determine the net result of all methylation processes at a given time and given conditions as opposed to searching for exact individual mechanisms and their significance to total methylmercury production. By comparing data from different parts of the river, it should be possible to determine which environmental factors affect methylmercury concentrations.

Work during the first year of the study was keyed to an examination of mercury and methylmercury dynamics and transport in the Wabigoon River between Dryden and the outlet of Clay Lake. This portion of the system contains a river, a reservoir, and a lake with a stratified and unstratified basin. In the second year, sampling was also conducted farther downsteam, from Clay Lake to the Manitoba border. Investigations into the role of suspended particulate matter on mercury cycling in the Wabigoon River were undertaken. Of particular interest was mercury resuspended and transported during high flows.

In 1978-79, crayfish, yellow perch, and young pike were collected from the river system from Wabigoon Lake to Eaglenest Lake on the Manitoba border to delineate geographical trends in mercury concentrations in these organisms. A study of mercury uptake by crayfish was also undertaken. In 1980, total and methyl mercury dynamics in the Wabigoon River between Dryden and Clay Lake were examined. Sediment cores were collected in the summer of 1980 from the major basins in the system and from the Wabigoon River between Dryden and Clay Lake. From these data, spatial and temporal trends for total mercury in sediments were assessed.

The results of these studies in conjunction with data from other investigators provide a basis for an elementary model covering key factors in mercury cycling in this river system. This basic understanding led to a review of amelioration proposals outlined in the progress report issued in 1980.

Section 2 is a description of the study area, including information on streamflow hydrology, physical and chemical limnology, and sediments. In section 3, profile data on mercury levels in sediments are presented to define the extent and degree of mercury enrichment in surface sediments. In section 4, total mercury and methylmercury dynamics and loadings in the river-lake system are examined. Key factors affecting total and methylmercury levels in water are identified. Section 5 presents biological data for adult walleye and pike. To document current biological contamination, young-of-the-year and yearling pike, perch, and crayfish were collected. Results of these surveys also delineate the geographical areas of concern. Included in section 5 are results of an experiment to distinguish the relative importance of mercury in food or water to mercury levels in crayfish. In section 6, empirical relationships between mercury concentrations in sediment, water and selected biota are described. Factors affecting mercury levels in biota are identified and assessed. Section 7 deals with the effects of current industrial discharges on mercury levels and cycling in the receiving stream. In section 8, the current state of the system is reviewed and amelioration methods identified. A semi-quantitative model is developed for assessing the usefulness of various amelioration schemes.

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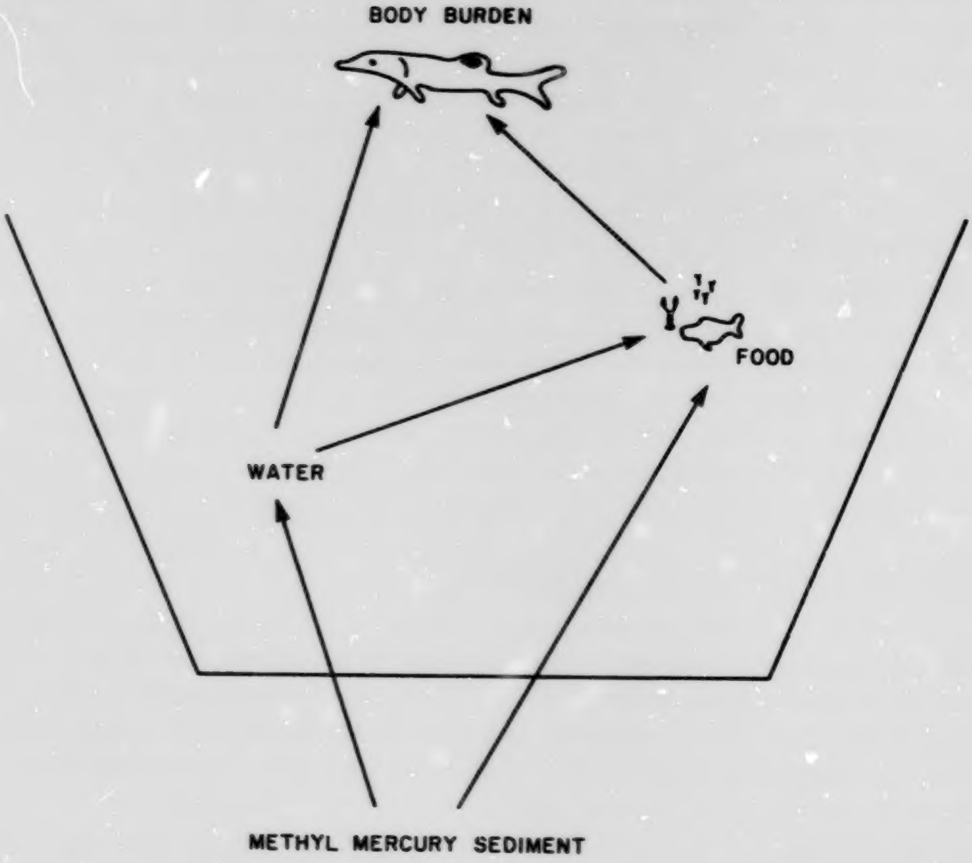
BODY BURDEN
FOOD
WATER
METHYL MERCURY SEDIMENT

Figure 1.1 A simple model of the pathways of methylmercury to predatory fish at the top of the food chain.

2. DESCRIPTION OF STUDY AREA

2.1 STREAMFLOW HYDROLOGY

(a) Wabigoon/English River System

This river system is located in northwestern Ontario, 300 km northwest of Thunder Bay, and extends from the Dryden to the Ontario-Manitoba border (Figure 2.1). The Wabigoon River joins the English River at Ball Lake and the English River joins the Winnipeg River at Tetu Lake. Total drainage area of the English River upstream of Caribou Falls (near Tetu Lake) is about 52,300 km^2 (square kilometres), and includes the Wabigoon River watershed of about 12,100 km^2. Flows in the English River are regulated by Ontario Hydro's generating stations at Caribou Falls, Manitou Falls and Ear Falls. Wabigoon River discharges are controlled by generating stations operated by Great Lakes Forest Products Limited at Eagle River and Dryden.

From July, 1979 to June, 1980, the Wabigoon River contributed 6 percent of the total flow at Tetu Lake. The English River contributed 51 percent and the Winnipeg River 43 percent. Mean annual flow of the English River at Caribou Falls from 1959-1976 was 487 m^3/s (cubic metres per second), compared with a mean flow of 451 m^3/s between July, 1979 and June, 1980. Mean monthly flows at selected sites are shown in Figure 2.2. Controlled flows are atypical of unregulated runoff. For example, most of the spring runoff in 1980 was retained in the system because of low precipitation in early 1980.

(b) Wabigoon River, Dryden to Clay Lake

Figure 2.3 illustrates the Wabigoon River and its tributary, the Eagle River, from Dryden to Clay Lake. Total drainage area of the Wabigoon River to the mouth of Clay Lake is approximately 6800 km^2, and comprises three major sub-basins. Wabigoon Lake and Eagle Lake are regulated by generating stations and the watershed downstream of these stations is unregulated. Sub-basin drainage areas and mean annual streamflows are presented in Table 2.1. From July, 1979 to June, 1980, unregulated flows contributed 29 percent, the Eagle River 39 percent, Wabigoon Lake 28 percent, and Great Lakes Forest Products Limited effluents 4 percent of the total streamflow entering Clay Lake.

Hydrographs for the Wabigoon River at Dryden and Quibell, and for the Eagle River (Figure 2.4) demonstrate the influence of flow regulation. Since the Great Lakes Forest Products Limited effluent is not incorporated into the flows provided by Water Survey of Canada for the Wabigoon River at Dryden, 1.6 m^3/s was added to discharges at this site. The first of the twin peaks at Quibell for the spring freshet in 1978 and 1979 represents unregulated flow. After spring rains, however, the storage capacity of Wabigoon Lake was exceeded and the resultant spills in May, 1978 and June, 1979 were reflected in the second peak at Quibell. Because of drought in the spring of 1980, there was no release of excess stored water at Dryden; consequently, there was only one flow peak of unregulated runoff at Quibell that year.

Flow regimes during the study period are compared with historical records in Figures 2.5 and 2.6. Flows at Dryden in 1978 were near the long-term averages. In 1979, flows remained at normal discharges until April. To evaluate the effects of high flows, Great Lakes Forest Products Limited agreed to increase flows in May. Over a period of a few days, flows were increased to 90 m³/s, and by May 12, they were 75 percent of the highest flow on record. Flows for the rest of the year were 10 to 50 percent of normal. In May and June, 1980, flows were sharply reduced to a fraction of normal levels. Streamflows for the Wabigoon River during the study approached historical extremes. Information collected during these extremes was useful in predicting the long-term effects of mercury.

Flows at Quibell from January, 1978 to May, 1979 generally followed historical values but during the next 5 months were about 10 to 20 percent below long-term averages. Spring flows in 1980 were clearly subnormal: average discharges for May were 31 percent of the long-term mean of 88.3 m³/s. In June, flows were only 9.6 percent of the long-term mean of 80.4 m³/s. The highest flow during the study, recorded on April 27, 1979, was 149 m³/s, or 55 pecent of the maximum recorded daily flow period. Although flows during the first quarter of 1978, 1979 and 1980 were very similar, discharges during the second quarter were very different for the three years.

(c) River Morphology

The gradient of the Wabigoon River was surveyed in October, 1980 and is illustrated in Figure 2.7. Water surface elevations were tied into the nearest geodetic elevations provided by bench marks of the Ministry of Transportation and Communications, Water Survey of Canada, or Canadian National Railways. Although flows were unusually low at the time of the survey, the profile shows the steep gradient of the upper section, and the extremely gentle slope of 0.012 m/km (metres per kilometre) in the 40 km stretch between the Wainwright Dam and the falls at the Highway #105 crossing. After the 6 m drop at this point, the river falls gradually to Quibell Falls, where there is a further drop of 7 m.

Channel cross-sections were measured at several points along the river (Figure 2 .8). These cross-sections show deep, well defined, U-shaped channels. Cross-sectional areas and wetted perimeters increase with distance downstream (Figure 2.9). The Eagle River confluence, about 45 km downstream from Dryden, has a substantial effect on river morphology. Rock structures along the river act as natural dams.

Low flows have a small effect on the wetted perimeter at sites downstream of the Wainwright Dam. During the very low flows in the summer of 1980, wetted perimeters were at least 85 percent of values during normal flows.

(d) Time-of-Travel

Time-of-travel and velocity measurements were carried out during the week of August 4-10, 1980 (Draper, et al., 1980) under low streamflows, when the discharge at Quibell was 6.6 m^3/s. Time-of-travel studies were conducted by standard dye-dilution techniques (Rhodamine B). Velocities generally decreased with decreases in the slope of the water surface profile (Figure 2.10). Based on the velocities measured, a parcel of water would take approximately 27 days to travel from Wainwright Dam to the inflow to Clay Lake. Similar time-of-travel measurements carried out by the Ontario Water Resources Commission in 1968, revealed a 3-day travel time for the same distance at much higher flow rates of 53 m^3/s at Quibell. The mean annual flows are 45 m^3/s at Quibell and 12 m^3/s at Dryden.

2.2 PHYSICAL LIMNOLOGY

Clay Lake (Figure 2.11) encompasses 3,000 ha (hectares), has a volume of $2.4 \times 10^8 m^3$ and a mean depth of 8 m. The theoretical residence time calculated from prorated Quibell flow records is 57 days at an annual mean flow of 49 m^3/s (1953-1976), and is approximately 31 days using mean May flows. During drought conditions in 1980, the theoretical residence time for Clay Lake was three times longer in May and 10 times longer in June than the long-term values for these months. There is a western basin which stratifies and is dimictic (turns over twice a year), and an eastern basin which does not stratify.

Ball Lake (Figure 2.12) covers 2,700 ha and has a volume of $2.9 \times 10^8 m^3$. Ball Lake has a northern basin which receives the English River flow, and a southern basin, which serves as a mixing zone for the English and Wabigoon Rivers. Both basins are morphologically similar with maximum depths of about 28 m. The larger flows from the English River, coupled with the natural land constrictions between basins, appear to effectively block wind-driven currents from the southern basin from moving into the northern basin. In the northern basin, the mean theoretical residence time is 5 days, based on mean flows from July, 1979 to June, 1980. For the southern basin, it is 2.5 days.

Lount, Grassy Narrows and Tetu Lakes are less than 33 m in depth.

2.3 SEDIMENTS

The bed of the upper half of the Wabigoon River is blanketed by mercury-enriched wood wastes. Anaerobic decomposition of this organic material results in substantial gas production: it is not unusual to observe mats of these organic sediments (up to $1/m^2$ in size) rise intact to the water surface, presumably from gas entrained in the fibres. Natural sediments in the river consist mainly of clay and silt. A more complete physical description (German, 1969) and geochemical evaluation (Jackson, 1980) of these sediments is available. Most sediments in the Wabigoon/English/Winnipeg River system are composed of a few millimetres of loosely flocculated organic material overlying clay. A more complete description of Clay Lake sediments has been prepared by Jackson (1980) and Armstrong and Hamilton (1973). Ball Lake sediments have also been described by Jackson (1980).

2.4 WATER QUALITY

Water samples for general chemical analysis were collected concurrently with samples for mercury analysis. Temperature and dissolved oxygen (by the Hach method) were measured in the field. All samples were cooled with ice and transported to the laboratory within 24 hours. Water quality data for Clay Lake for the first year of the study were provided by Dr. J. W. M. Rudd, Freshwater Institute, Environment Canada, Winnipeg (methods given by Stainton, et al. 1977). Subsequent analyses were performed at the Ontario Ministry of the Environment Laboratory, Thunder Bay, (Ontario Ministry of the Environment, 1975).

All chemical analyses are summarized in Appendix 2-A. Appendix 2-B presents a correlation matrix of selected parameters for non-high flows at several sites. Water quality data for high flows, defined at those above 14 m^3/s at Dryden (Figure 2.5) and 56 m^3/s at Clay Lake (Figure 2.6), may be found in Jackson, et al. (1983). Selected analysis results for a 4-month period of relatively stable, typical hydraulic conditions are presented in Table 2.2.

Effluent from the pulp and paper making complex at Dryden has substantially degraded the physical and chemical characteristics of the receiving stream. Dilution of the Wabigoon River by the English River at Ball Lake, however, restores the system to near normal.

At control sites, mean values of suspended solids ranged from 2 mg/ℓ (milligrams of suspended solids per litre of water) at Sand Lake to 6 mg/ℓ at Wabigoon Lake. BOD_5 values were similar at all sites (0.6 mg/ℓ to 0.8 mg/ℓ). Wabigoon Lake has the darkest colour (52 Hazen units) and Eagle River the lightest (19 units). Wabigoon Lake was more turbid than the other control sites by a factor of about five, no doubt because of the large quantities of colloidal clay in its water. Waters at all control sites were slightly alkaline, with pH values ranging from 7.0 to 7.7. The effects of industrial discharges at Dryden are greatest on waters immediately downstream. Loadings from the sewage treatment plant at Dryden are minor in comparison to those from the industrial source, with the possible exception of phosphorus. Dissolved oxygen, sulphide, suspended solids, chloride, iron, manganese, BOD_5, and phosphorus may all affect mercury cycling in the Wabigoon.

Dissolved oxygen levels strongly affect water chemistry, microbiology, and exchange processes between sediment and water (Hutchinson, 1957) Dissolved oxygen concentrations in the Wabigoon exhibit a predictable response to heavy organic loadings (Figure 2.13). The dissolved oxygen deficit reaches its maximum in the Minnitaki area, with near recovery at Clay Lake. When mill operations were temporarily suspended in 1977, dissolved oxygen concentrations were still sharply depressed in much of the river. Dissolved oxygen levels were as low as 1.5 to 2 mg/ℓ in the Minnitaki area of the river, compared with levels of about 10 mg/ℓ at control sites. The geographical extent and severity of the dissolved oxygen depletion is mainly a function of organic loadings, water temperature and dilution by natural flows. During spring months, when flows are high and water temperatures are low, there are probably no anoxic conditions anywhere in the river. When flows dropped well below normal, as in 1980, and temperatures increased, anaerobic conditions increased until nearly the entire river from Dryden to Clay Lake was devoid of dissolved oxygen (Table 2.3).

Industrial loadings at Dryden directly affect concentrations of sulphur compounds, suspended solids, chloride, iron, and manganese (Appendix 2-A) which may influence the cycling of mercury in the river.

Measurements of free sulphide were not possible. Qualitative statements concerning levels of reduced sulphur compounds can be made, however, using odour as a guide. The strongest odour is present at the submerged industrial outfall at Dryden. During the ice-free period and under normal hydraulic conditions, there is little odour at the inflow to Clay Lake. At Clay Lake, increases in odour are evident during ice cover. Under the extreme low flow conditions in the summer of 1980, odour increased sharply at all downstream river sites, including the inflow to Clay Lake.

Suspended solids concentrations are presented in Table 2.4. Suspended solids loadings from the industrial source at Dryden raised levels in the receiving stream from 4.7 mg/ℓ in Wabigoon Lake to 20 mg/ℓ at the inflow to the Wainwright Dam. The Wainwright Dam may act as a very slight trap for some particulate matter, since suspended solids declined slightly to 17 mg/ℓ at the dam outflow. At the inflow to Clay Lake, suspended solids concentrations averaged 12 mg/ℓ, and decreased sharply to 2.7 mg/ℓ at the outflow. The effect of flow on suspended solids concentrations at Wainwright Dam and Minnitaki for non-high flow events is shown in Figures 2.14 to 2.16. The relationship was inverse, perhaps due to the dilution of mill wastes. There was similar relationship at the inflow to Clay Lake (Figure 2.17). Figure 2.17 also includes results during the 1980 spring runoff. The positive correlation between flow and suspended solids suggests that during periods of high flow, suspended solids concentrations increase. The inverse relationship between flow and suspended solids indicates that resuspension of sediments is not an important process during non-high flows. During controlled floods, resuspended sediments in the upper Wabigoon River result in concentrations of 140 mg/ℓ at the inflow to Wainwright Dam and 210 mg/ℓ at Minnitaki. Peak suspended solids concentrations are about 15 mg/ℓ during the spring runoff at the inflow to Clay Lake. Most of the material resuspended at the Wainwright Dam settles upstream of Clay Lake, as expected for a river with a gentle gradient.

Anthropogenic inputs of two kinds of nutrients at Dryden also affect the receiving stream. Soluble organic compounds stimulate microbial populations in the water, resulting in total coliform counts near the industrial discharge to be several orders of magnitude above control values. These organic loadings are responsible for the loss of dissolved oxygen through microbial oxidation and are almost totally oxidized by the time river waters reach Clay Lake. Inorganic nutrients discharged at Dryden, such as phosphorus, are not considered to be of particular concern in the river but may accelerate the eutrophication process in Clay Lake.

The effects of industrial discharges at Dryden on water quality have been fairly uniform over the past 10 years, as shown by data for chloride and suspended solids in Figures 2.18 and 2.19. Their fluctuations were generally random, with the exception of 1977 and 1980. Elevated concentrations during these years were due to low flows, when the quantity of water available for dilution of mill waste was substantially reduced. Levels of conservative parameters such as chloride are reduced in the receiving stream by dilution of incoming clean flows. At the inflow to Clay Lake, chloride levels were approximately one-third the values at Dryden.

Under typical hydrological conditions, the untreated wastes from the mill complex formed 10-15 percent of the Wabigoon River flows downstream of Dryden. Sharp fluctuations in waste quality could create substantial short-term changes in downstream river quality. Under typical flows of 12.5 m^3/s, wastes are well mixed laterally and vertically, but not longitudinally, at the inflow to Wainwright Dam. The variance associated with short-term fluctuations in chemicals in mill wastes decreased progressively downstream. Large, short-term fluctuations were rarely evident at Clay Lake.

The high biological productivity of Clay Lake is probably responsible for anaerobic conditions in hypolimnetic waters in its western basin in late summer and winter. Concommitant changes in water chemistry in the hypolimnion during anaerobic conditions include elevated iron and phosphorus. Sulphide was below the detection limit (<10 μg/l) in hypolimnion samples analyzed in September, 1979. High iron concentrations are probably responsible for low sulphide concentrations, since iron sulphide is present in sediments (Furutani and Rudd, 1980). Low sulphide levels in other lakes in the Canadian shield with similar iron levels have been attributed to sulphide removal through iron sulphide formation (Schindler, et al., 1980).

In Ball Lake, the entire water column generally remained well mixed and oxygenated throughout the year.

2.5 GEOLOGY

Discontinuous Pleistocene deposits of glaciolacustrine material cover most of the watershed with limited outcrops of bare Precambrian bedrock in some areas. Deposits are predominantly clay and silt, with some sandy till. Morainic sand ridges and outwash sand plains occur in the Eagle Lake watershed (Zoltai, 1974). Bedrock consists of acid igneous and metamorphic rocks with metavolcanics and some metasediments forming significant portions of the Eagle and Wabigoon Lake basins.

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TABLE 2.1. Drainage areas and mean annual flows of major sub-watersheds of the Wabigoon River above Clay Lake.

Watershed	Drainage Area (km^2)	Mean Annual Flow[a] (m^3/s)	Mean Annual Flow[a] % of Total	Flow Range (m^3/s)
Wabigoon Lake	2200	11.8	26.5	0-121
Eagle Lake	2500	15.7	35.3	0- 90
Unregulated watershed upstream of Clay Lake	2100	17.0	38.2	11-235[b]
TOTAL	6800	44.5	100.0	

[a] Average from 1972 to 1979.

[b] Wabigoon River at Quibell.

TABLE 2.2. Average levels and ranges of selected water quality parameters in the Wabigoon/English/Winnipeg River system, July-October, 1979, (July 10, August 2, September 4 and October 2).

Site[a]	pH	Total Solids (mg/ℓ)	Suspended Solids (mg/ℓ)	BOD_5 (mg/ℓ)	Cl (mg/ℓ)	Colour (Hazen)	Turbidity (Formazin)
1. Wabigoon Lake	7.7[b] 7.6-7.7[c]	82 80-85	6 5-9	.7 0.6-0.8	1 1.0-1.1	52 40-60	15 10-18
2. Eagle River	7.0 6.7-7.2	43 32-57	4 3-5	0.6 0.3-1.2	1.1 0.4-2.0	19 15-30	3.1 2.7-3.7
3. G.L.F.P. Limited	6.5 4.9-7.3	480 250-710	127 70-170	100 44-130	135 14-276	280 70-600	55 37-80
4. Inflow to Wainwright Dam	7.5 6.2-9.4	320 285-355	29 18-39	24 15-36	32 12-64	118 50-200	25 21-28
5. Outflow of Wainwright Dam	7.1 6.1-8.3	378 280-475	23 17-35	19 11-29	24 0.5-36	145 60-300	24 21-27
6. At Minnitaki	5.9 4.4-6.5	227 205-245	16 14-20	13 65-180	34 27-40	130 70-150	17.7 1.8-2.8
7. Clay Lake Inflow	6.8 6.7-6.9	108 105-115	15 15-16	12 10-14	11 5-15	68 60-80	16 14-17
10. Clay Lake Outflow	7.3 7.1-7.5	106 89-118	2 1-2	0.6 0.4-1.0	9 7-10	60 50-70	3.1 2.3-4.7
11. Wabigoon River Inflow to Ball Lake	7.3 7.1-7.4	108 95-130	4 3-5	0.8 0.7-0.8	7 4-9	60	4.6 3.9-5.3

TABLE 2.2. (Continued).

Site[a]	pH	Total Solids (mg/ℓ)	Suspended Solids (mg/ℓ)	BOD$_5$ (mg/ℓ)	Cl (mg/ℓ)	Colour (Hazen)	Turbidity (Formazin)
12. English River Inflow to Ball Lake	7.6 7.4-7.8	82 70-100	4 2-5	0.7 0.4-1.1	1 .05-2	38 30-50	3.7 3.3-4.2
13. English River Outflow of Ball Lake	7.4 7.3-7.5	83 70-100	2 1.5-2	0.6 0.4-0.8	2 1-3	42 30-50	3.1 2.1-4.2
14. Lount Lake	7.4 7.2-7.6	85 80-90	4 3-5	0.8 0.6-0.9	2 1-3	38 30-40	3.3 2.1-3.8
15. Umfreville Lake	7.4 7.3-7.6	67 65-70	1 1.5-2	0.5 0.2-0.7	3 2-5	40	1.6 1.3-2.2
16. Sand Lake	7.5 7.4-7.7	81 70-90	2 1.5-3	0.8 0.6-1.0	2 2-3	30	1.9 1.5-2.2
17. Eaglenest Lake	7.5 7.3-7.6	90 80-100	3	0.7 0.6-1.0	2 2-3	30	2.0 1.5-2.4

[a] See Figure 2.1.

[b] Mean.

[c] Range.

TABLE 2.3. Dissolved oxygen concentrations (mg/ℓ) at selected sites in the Wabigoon River, May-June, 1980.

Site	Date (1980)					
	May 5-6	May 20-21	Jun 2-3	Jun 9-10	Jun 16-17	Jun 23-24
Wabigoon Lake					9.0	
Inflow to Wainwright Dam					0	0
Outflow of Wainwright Dam					0	0
At Minnitaki			0	0	0	0
Upstream of Eagle River Confluence	2.6	0	0	0	0	0
Eagle River		9.2	7.4	9.2	9.0	9.5
3.1 km Downstream of Eagle River	4.5	1.8	0	0	0	0
9.8 km Downstream of Eagle River	4.8	1.4	0	0	0	0
At Red Lake, Highway #105			0.15		0	0
Inflow to Clay Lake			4.5	5.3	2.4	0.9

TABLE 2.4. Suspended solids concentrations in the Wabigoon River system, 1978-80.

Site	N[b]	Mean (mg/ℓ)	Standard Deviation	Range
Wabigoon Lake	19	4.7	2.0	1.0-9.0
Wainwright Dam, inflow[a]	19	20	6.6	15-39
Wainwright Dam, outflow[a]	19	17	7.9	9-35
Minnitaki[a]	12	21	17	5.0-69
Clay Lake, inflow	24	12	5.8	5.0-30
Clay Lake, eastern basin	23	7.1	3.3	2.0-18
Clay Lake, western basin	24	2.7	1.2	1.0-5.0
Clay Lake, outflow	25	2.7	1.2	1.0-5.0

[a] During non-high flow periods only.

[b] Number of samples.

APPENDIX 2-A

WATER QUALITY DATA SUMMARIES FOR NON-HIGH FLOW PERIODS

Site	Temperature (°C)			
	N	Mean	Std. Dev.	Range
Wabigoon Lake	54	11	7.4	0.10-22
Wainwright Dam - Inflow	54	13	7.9	0.50-28
Wainwright Dam - Outflow	54	12	7.9	0.40-26
Minnitaki	33	14	7.9	0.50-24
Clay Lake - Inflow	62	12	8.0	0.0-25
Clay Lake - East Basin	52	12	8.2	0.0-25
Clay Lake - West Basin	54	12	7.8	0.0-23
Clay Lake - Outflow	44	11	8.1	0.0-24
Wabigoon - Inflow to Ball Lake	13	8.1	8.8	0.20-22
Eagle River	22	15	6.4	0.0-22

Site	pH			
	N	Mean	Std. Dev.	Range
Wabigoon Lake	25	7.6	0.40	6.5-8.3
Wainwright Dam - Inflow	25	7.1	1.1	3.3-9.4
Wainwright Dam - Outflow	25	6.9	0.66	5.3-8.3
Minnitaki	25	6.6	0.60	4.4-7.5
Clay Lake - Inflow	24	6.9	0.32	6.4-7.6
Clay Lake - East Basin	26	7.2	0.31	6.7-7.8
Clay Lake - West Basin	27	7.2	0.39	6.7-8.3
Clay Lake - Outflow	27	7.2	0.37	6.5-7.8
Wabigoon - Inflow to Ball Lake	11	7.0	0.32	6.6-7.4
Eagle River	29	7.1	0.57	5.8-8.1

Site	Conductivity (µmhos/cm) N	Mean	Std. Dev.	Range
Wabigoon Lake	30	92	15	60-114
Wainwright Dam - Inflow	29	290	159	108-720
Wainwright Dam - Outflow	30	303	169	103-750
Minnitaki	31	235	74	127-450
Clay Lake - Inflow	26	145	28	97-201
Clay Lake - East Basin	30	133	16	97-175
Clay Lake - West Basin	30	126	23	80-200
Clay Lake - Outflow	31	125	22	80-200
Wabigoon - Inflow to Ball Lake	12	123	18	97-145
Eagle River	29	48	6.6	35-65

Site	Suspended Solids (mg/ℓ) N	Mean	Std. Dev.	Range
Wabigoon Lake	19	4.7	2.0	1.0-9.0
Wainwright Dam - Inflow	19	20	6.6	15-39
Wainwright Dam - Outflow	19	17	7.9	9.0-35
Minnitaki	12	21	17	5.0-69
Clay Lake - Inflow	24	12	5.8	5.0-30
Clay Lake - East Basin	23	7.1	3.3	2.0-18
Clay Lake - West Basin	24	2.7	1.2	1.0-5.0
Clay Lake - Outflow	25	2.7	1.2	1.0-5.0
Wabigoon - Inflow to Ball Lake	10	8.4	16	2.0-55
Eagle River	13	3.8	2.2	1.0-10

Site	Chloride (mg/ℓ) N	Mean	Std. Dev.	Range
Wabigoon Lake	15	1.4	0.37	0.9-2.0
Wainwright Dam - Inflow	15	37	27	12-117
Wainwright Dam - Outflow	15	40	26	5.0-114
Minnitaki	12	31	13	8.0-59
Clay Lake - Inflow	10	14	4.2	5.0-17
Clay Lake - East Basin	13	12	2.5	7.6-15
Clay Lake - West Basin	8	11	3.5	6.5-17
Clay Lake - Outflow	11	9.8	4.1	0.0-15
Wabigoon - Inflow to Ball Lake	11	9.5	3.1	4.0-13
Eagle River	13	1.3	1.5	0.40-6.0

Site	SO_4 (mg/ℓ) N	Mean	Std. Dev.	Range
Wabigoon Lake	20	3.8	1.2	1.4-7.0
Wainwright Dam - Inflow	20	28	26	8.1-115
Wainwright Dam - Outflow	20	29	30	9.4-145
Minnitaki	13	18	7.8	3.9-33
Clay Lake - Inflow	28	12	5.7	5.8-33
Clay Lake - East Basin	26	11	2.6	6.0-17
Clay Lake - West Basin	27	10	3.2	5.1-18
Clay Lake - Outflow	26	9.7	3.0	6.1-19.4
Wabigoon - Inflow to Ball Lake	11	7.9	1.8	4.2-10
Eagle River	14	3.2	0.80	1.2-4.4

Site	Fe (mg/ℓ)			
	N	Mean	Std. Dev.	Range
Wabigoon Lake	10	0.76	0.36	0.06-1.3
Wainwright Dam - Inflow	10	1.1	0.36	0.44-1.7
Wainwright Dam - Outflow	10	0.97	0.33	0.48-1.5
Minnitaki	11	1.1	0.52	0.10-1.8
Clay Lake - Inflow	9	0.87	0.60	0.11-2.1
Clay Lake - East Basin	7	0.51	0.26	0.22-0.98
Clay Lake - West Basin	8	0.44	0.21	0.19-0.79
Clay Lake - Outflow	9	0.48	0.23	0.16-0.86
Wabigoon - Inflow to Ball Lake	11	0.47	0.17	0.22-0.84
Eagle River	11	1.0	2.0	0.02-5.2

Site	Mn (μg/ℓ)			
	N	Mean	Std. Dev.	Range
Wabigoon Lake	9	12.9	3.8	8.0-17
Wainwright Dam - Inflow	9	77	41	29-170
Wainwright Dam - Outflow	9	77	44	38-180
Minnitaki	10	70	21	49-110
Clay Lake - Inflow	9	47	27	14-93
Clay Lake - East Basin	7	32	6.9	19-40
Clay Lake - West Basin	8	38	19	15-70
Clay Lake - Outflow	8	32	17	15-57
Wabigoon - Inflow to Ball Lake	10	34	17	8.0-64
Eagle River	10	8.1	6.5	2.0-20

Site	Total Phosphorus (µg/ℓ)			
	N	Mean	Std. Dev.	Range
Wabigoon Lake	11	27	3.4	3-16
Wainwright Dam - Inflow	11	63	9.8	45-79
Wainwright Dam - Outflow	10	66	10.2	47-82
Minnitaki	3	79	22	64-104
Clay Lake - Inflow	20	42	12	31-84
Clay Lake - East Basin	17	40	10	28-65
Clay Lake - West Basin	22	21	11	5.0-42
Clay Lake - Outflow	18	38	14	23-68
Wabigoon - Inflow to Ball Lake	-	-	-	-
Eagle River	4	18	3.4	15-23

Site	Turbidity (Formazin Units)			
	N	Mean	Std. Dev.	Range
Wabigoon Lake	10	14	2.9	9.9-18
Wainwright Dam - Inflow	10	23	10	15-50
Wainwright Dam - Outflow	10	23	11	15-53
Minnitaki	11	22	13	1.8-46
Clay Lake - Inflow	10	14	6.1	5.8-24
Clay Lake - East Basin	8	9.5	3.2	5.8-15
Clay Lake - West Basin	9	4.5	2.0	2.1-8.1
Clay Lake - Outflow	9	4.4	2.1	1.9-7.6
Wabigoon - Inflow to Ball Lake	11	4.4	0.56	3.6-5.3
Eagle River	11	3.7	2.4	0.80-9.0

Site	Alkalinity (mg/ℓ)			
	N	Mean	Std. Dev.	Range
Wabigoon Lake	10	44	1.3	42-46
Wainwright Dam - Inflow	10	46	31	0.0-114
Wainwright Dam - Outflow	10	46	34	13-135
Minnitaki	11	45	21	0.0-83
Clay Lake - Inflow	10	37	3.9	31-44
Clay Lake - East Basin	8	31	3.2	31-39
Clay Lake - West Basin	9	34	5.6	21-41
Clay Lake - Outflow	9	36	[illegible]	32-40
Wabigoon - Inflow to Ball Lake	11	36	1.5	35-38
Eagle River	11	22	5.5	18-38

Site	Hardness (mg/ℓ)			
	N	Mean	Std. Dev.	Range
Wabigoon Lake	10	45	2.5	42-50
Wainwright Dam - Inflow	9	55	6.5	48-71
Wainwright Dam - Outflow	9	56	6.2	50-71
Minnitaki	10	60	7.0	52-76
Clay Lake - Inflow	9	41	4.4	37-49
Clay Lake - East Basin	7	40	5.1	34-48
Clay Lake - West Basin	8	40	1.4	39-43
Clay Lake - Outflow	8	40	2.0	37-43
Wabigoon - Inflow to Ball Lake	10	42	6.5	38-60
Eagle River	10	20	2.0	18-25

Site	BOD$_5$ (mg/ℓ)			
	N	Mean	Std. Dev.	Range
Wabigoon Lake	9	0.10	0.22	0.20-0.80
Wainwright Dam - Inflow	9	28	21	1.5-65
Wainwright Dam - Outflow	9	21	11	7.0-35
Minnitaki	10	17	8.6	5.0-30
Clay Lake - Inflow	10	2.1	1.8	0.60-6.5
Clay Lake - East Basin	8	1.8	1.2	1.1-4.2
Clay Lake - West Basin	9	1.8	2.9	0.40-9.0
Clay Lake - Outflow	9	1.2	1.3	0.2-4.4
Wabigoon - Inflow to Ball Lake	11	0.91	0.53	0.20-2.2
Eagle River	10	0.73	0.59	0.20-1.8

Site	Al (μg/ℓ)			
	N	Mean	Std. Dev.	Range
Wabigoon Lake	9	1052	162	800-1300
Wainwright Dam - Inflow	9	1107	502	280-1800
Wainwright Dam - Outflow	9	1125	423	390-1700
Minnitaki	10	1176	482	290-1900
Clay Lake - Inflow	9	850	530	170-2000
Clay Lake - East Basin	7	1259	1662	360-5000
Clay Lake - West Basin	8	1118	1456	180-4500
Clay Lake - Outflow	8	1778	2173	160-5300
Wabigoon - Inflow to Ball Lake	10	373	130	180-660
Eagle River	10	133	144	23-520

Site	Chlorophyll ā (μg/ℓ)			
	N	Mean	Std. Dev.	Range
Wabigoon Lake	11	3.8	3.2	0.40-10.5
Wainwright Dam - Inflow	11	2.7	2.1	0.30-6.3
Wainwright Dam - Outflow	12	2.3	2.4	0.0-7.9
Minnitaki	3	1.5	1.0	0.40-2.3
Clay Lake - Inflow	14	3.3	3.5	0.50-14
Clay Lake - East Basin	15	13	24	0.40-96
Clay Lake - West Basin	15	9.9	25	0.30-100
Clay Lake - Outflow	16	4.2	5.3	0.30-22
Wabigoon - Inflow to Ball Lake	-	-	-	-
Eagle River	4	2.6	1.5	0.80-4.3

APPENDIX 2-B

CORRELATION MATRICES FOR SELECTED WATER QUALITY PARAMETERS

APPENDIX 2-B.1 Wabigoon Lake.

		TEMP	Ph	COND	CHL-A	Cl	SO_4	Na	Fe	TDS	TSS	TOT.P	TURB	BOD	Mn
TEMP	R	1.000													
	n	0.000													
	p	0.000													
pH	R	0.499	1.000												
	n	25.000	0.000												
	p	0.000	0.000												
COND	R	-.288	0.154	1.000											
	n	30.000	25.000	0.000											
	p	0.129	0.461	0.000											
CHL-A	R	0.790	0.317	-.749	1.000										
	n	11.000	10.000	10.000	0.000										
	p	0.000	0.373	0.000	0.000										
Cl	R	0.313	0.386	0.168	0.226	1.000									
	n	15.000	15.000	15.000	6.000	0.000									
	p	0.260	0.155	0.550	0.666	0.000									
SO_4	R	-.161	-.161	0.247	0.233	0.372	1.000								
	n	20.000	19.000	19.000	11.000	15.000	0.000								
	p	0.497	0.511	0.308	0.490	0.173	0.000								
Na	R	-.626	-.081	0.392	0.468	0.273	0.283	1.000							
	n	20.000	19.000	19.000	11.000	15.000	20.000	0.000							
	p	0.000	0.742	0.097	0.146	0.325	0.226	0.000							
Fe	R	-.052	-.113	-.619	0.000	-.487	-.656	-.332	1.000						
	n	10.000	10.000	10.000	0.000	10.000	10.000	10.000	0.000						
	p	0.886	0.756	0.056	0.000	0.154	0.000	0.319	0.000						
TDS	R	-.369	-.456	0.375	0.000	0.245	0.857	0.512	0.693	1.000					
	n	8.000	8.000	8.000	0.000	8.000	8.000	8.000	8.000	0.000					
	p	0.369	0.257	0.360	0.000	0.559	0.000	0.194	0.055	0.000					
TSS	R	0.646	0.533	-.237	0.580	0.281	-.082	-.225	0.257	-.267	1.000				
	n	19.000	18.000	18.000	10.000	15.000	19.000	19.000	10.000	8.000	0.000				
	p	0.000	0.000	0.345	0.079	0.311	0.311	0.354	0.473	0.523	0.000				
TOT.P	R	0.655	0.257	-.610	0.724	0.000	0.579	-.552	0.000	0.000	0.646	1.000			
	n	11.000	10.000	10.000	11.000	6.000	11.000	11.000	0.000	0.000	10.000	0.000			
	p	0.000	0.474	0.061	0.000	1.000	0.062	0.078	0.000	0.000	1.000	0.000			
TURB	R	0.310	0.056	-.245	0.000	-.126	-.348	-.429	0.389	-.293	0.521	0.000	1.000		
	n	10.000	10.000	10.000	0.000	10.000	10.000	10.000	10.000	8.000	10.000	0.000	0.000		
	p	0.383	0.878	0.495	0.000	0.730	0.325	0.216	0.266	0.482	0.123	0.000	0.000		
BOD	R	0.259	0.210	0.362	0.000	0.573	0.469	0.065	-.578	0.298	0.048	0.000	0.284	1.000	
	n	9.000	9.000	9.000	0.000	9.000	9.000	9.000	9.000	7.000	9.000	0.000	9.000	0.000	
	p	0.500	0.587	0.339	0.000	0.107	0.203	0.869	0.103	0.517	0.901	0.000	0.458	0.000	
Mn	R	0.785	0.348	-.492	0.000	-.150	-.632	-.814	0.441	-.409	0.932	0.000	0.788	0.068	1.000
	n	9.000	9.000	9.000	0.000	9.000	9.000	9.000	9.000	8.000	9.000	0.000	9.000	8.000	0.872
	p	0.000	0.359	0.178	0.000	0.700	0.068	0.000	0.235	0.314	0.000	0.000	0.000	0.872	0.000

APPENDIX 2-B.1 Eagle River.

		TEMP	Ph	COND	CHL-A	Cl	SO_4	Na	Fe	TDS	TSS	TOT.P	TURB	BOD	Mn
TEMP	R	1.000													
	n	0.000													
	p	0.000													
pH	R	0.473	1.000												
	n	20.000	0.000												
	p	0.000	0.000												
COND	R	0.276	0.257	1.000											
	n	21.000	27.000	0.000											
	p	0.226	0.195	0.000											
CHL-A	R	-.674	-.135	-.796	1.000										
	n	3.000	4.000	4.000	0.000										
	p	0.529	0.865	0.204	0.000										
Cl	R	-.595	-.443	-.363	-.454	1.000									
	n	7.000	13.000	13.000	3.000	0.000									
	p	0.159	0.130	0.223	0.700	0.000									
SO_4	R	-.002	-.130	0.724	0.821	0.138	1.000								
	n	7.000	14.000	14.000	4.000	13.000	0.000								
	p	0.996	0.659	0.000	0.179	0.654	0.000								
Na	R	-.620	-.486	-.265	-.170	0.939	0.196	1.000							
	n	7.000	14.000	14.000	4.000	13.000	14.000	0.000							
	p	0.137	0.078	0.359	0.830	0.000	0.502	0.000							
Fe	R	0.409	0.101	0.272	0.000	-.163	-.101	-.093	1.000						
	n	5.000	11.000	11.000	1.000	11.000	11.000	11.000	0.000						
	p	0.494	0.768	0.419	0.000	0.632	0.769	0.786	0.000						
TDS	R	0.467	0.082	0.690	0.000	0.581	-.462	-.470	0.723	1.000					
	n	4.000	10.000	10.000	0.000	10.000	10.000	10.000	10.000	0.000					
	p	0.533	0.821	0.000	0.000	0.078	0.179	0.171	0.000	0.000					
TSS	R	-.209	0.095	0.255	0.891	0.018	-.242	-.609	0.845	0.620	1.000				
	n	7.000	13.000	13.000	3.000	13.000	13.000	13.000	11.000	10.000	0.000				
	p	0.653	0.759	0.401	0.300	0.954	0.425	0.976	0.000	0.056	0.000				
TOT.P	R	0.007	-.230	-.637	0.160	0.933	0.555	-.588	0.000	0.000	-.359	1.000			
	n	3.000	4.000	4.000	4.000	3.000	4.000	4.000	0.000	0.000	3.000	0.000			
	p	0.995	0.770	0.363	0.840	0.234	0.445	0.412	0.000	0.000	0.766	0.000			
TURB	R	0.954	0.000	0.332	0.000	-.271	0.192	-.172	0.384	0.448	0.321	0.000	1.000		
	n	5.000	11.000	11.000	0.000	11.000	11.000	11.000	11.000	10.000	11.000	0.000	0.000		
	p	0.000	1.000	0.319	0.000	0.420	0.573	0.614	0.243	0.194	0.336	0.000	0.000		
BOD	R	-.995	-.537	0.071	0.000	0.620	-.144	0.650	0.164	0.063	0.426	0.000	-.253	1.000	
	n	5.000	10.000	10.000	0.000	10.000	10.000	10.000	10.000	9.000	10.000	0.000	10.000	0.000	
	p	0.000	0.109	0.845	0.000	0.056	0.690	0.000	0.650	0.872	0.220	0.000	0.482	0.000	
Mn	R	0.839	-.175	0.502	0.000	-.089	-.166	-.070	0.924	0.642	0.774	0.000	0.353	0.196	1.000
	n	4.000	10.000	10.000	0.000	10.000	10.000	10.000	10.000	10.000	10.000	0.000	10.000	9.000	0.000
	p	0.161	0.629	0.139	0.000	0.808	0.647	0.848	0.000	0.050	0.000	0.000	0.317	0.614	0.000

APPENDIX 2-B.1 Effluent from Great Lakes Forest Products Limited.

		TEMP	Ph	COND	CHL-A	Cl	SO_4	Na	Fe	TDS	TSS	TOT.P	TURB	BOD	Mn
TEMP	R	1.000													
	n	0.000													
	p	0.000													
pH	R	0.000	1.000												
	n	0.000	0.000												
	p	0.000	0.000												
COND	R	0.000	0.333	1.000											
	n	0.000	6.000	0.000											
	p	0.000	0.519	0.000											
CHL-A	R	0.000	-.129	0.000	1.000										
	n	0.000	7.000	0.000	0.000										
	p	0.000	0.782	0.000	0.000										
Cl	R	0.000	-.837	-.176	-.038	1.000									
	n	0.000	10.000	5.000	5.000	0.000									
	p	0.000	0.000	0.777	0.952	0.000									
SO_4	R	0.000	-.500	0.819	-.086	0.661	1.000								
	n	0.000	12.000	6.000	8.000	11.000	0.000								
	p	0.000	0.097	0.050	0.839	0.000	0.000								
Na	R	0.000	-.381	0.430	0.115	0.701	0.648	1.000							
	n	0.000	12.000	6.000	8.000	11.000	14.000	0.000							
	p	0.000	0.222	0.394	0.786	0.000	0.000	0.000							
Fe	R	0.000	0.614	0.590	0.000	-.243	0.773	0.659	1.000						
	n	0.000	6.000	5.000	1.000	7.000	7.000	7.000	0.000						
	p	0.000	0.195	0.295	0.000	0.599	0.000	0.107	0.000						
TDS	R	0.000	0.034	0.634	0.000	0.261	0.498	0.968	0.621	1.000					
	n	0.000	5.000	4.000	0.000	6.000	6.000	6.000	6.000	0.000					
	p	0.000	0.956	0.366	0.000	0.617	0.314	0.000	0.188	0.000					
TSS	R	0.000	0.572	0.728	-.271	-.272	0.041	0.372	0.981	0.651	1.000				
	n	0.000	11.000	6.000	7.000	11.000	13.000	13.000	7.000	6.000	0.000				
	p	0.000	0.066	0.101	0.556	0.418	0.894	0.211	0.000	0.161	0.000				
TOT.P	R	0.000	-.582	1.000	-.256	0.971	0.869	0.888	0.000	0.000	-.058	1.000			
	n	0.000	7.000	2.000	8.000	5.000	8.000	8.000	1.000	0.000	7.000	0.000			
	p	0.000	0.171	0.000	0.541	0.000	0.000	0.000	0.000	0.000	0.901	0.000			
TURB	R	0.000	-.020	-.648	0.000	-.247	-.416	-.540	-.146	-.588	-.261	0.000	1.000		
	n	0.000	6.000	5.000	1.000	7.000	7.000	7.000	7.000	6.000	7.000	0.000	0.000		
	p	0.000	0.970	0.236	0.000	0.594	0.354	0.211	0.755	0.220	0.572	0.000	0.000		
BOD	R	0.000	0.132	0.875	0.000	0.645	0.528	0.812	0.570	0.795	0.598	0.000	-.502	1.000	
	n	0.000	5.000	4.000	1.000	6.000	6.000	6.000	6.000	5.000	6.000	1.000	6.000	0.000	
	p	0.000	0.833	0.125	0.000	0.166	0.282	0.050	0.238	0.108	0.210	0.000	0.311	0.000	
Mn	R	0.000	-.321	-.551	0.000	0.721	-.471	0.088	-.074	-.081	-.194	0.000	0.449	0.626	1.000
	n	0.000	5.000	4.000	0.000	6.000	6.000	6.000	6.000	6.000	6.000	0.000	6.000	5.000	0.000
	p	0.000	0.598	0.449	0.000	0.106	0.346	0.868	0.890	0.879	0.713	0.000	0.372	0.258	0.000

APPENDIX 2-B.1 Inflow to Wainwright Dam.

		TEMP	Ph	COND	CHL-A	Cl	SO_4	Na	Fe	TDS	TSS	TOT.P	TURB	BOD	Mn
TEMP	R	1.000													
	n	0.000													
	p	0.000													
pH	R	-.211	1.000												
	n	25.000	0.000												
	p	0.312	0.000												
COND	R	0.371	-.354	1.000											
	n	29.000	24.000	0.000											
	p	0.047	0.089	0.000											
CHL-A	R	0.860	-.302	-.287	1.000										
	n	11.000	10.000	10.000	0.000										
	p	0.000	0.396	0.421	0.000										
Cl	R	0.104	-.779	0.601	-.057	1.000									
	n	15.000	15.000	14.000	6.000	0.000									
	p	0.712	0.000	0.000	0.915	0.000									
SO_4	R	0.144	0.062	0.790	-.700	0.271	1.000								
	n	20.000	19.000	18.000	11.000	15.000	0.000								
	p	0.544	0.801	0.000	0.000	0.328	0.000								
Na	R	0.055	0.097	0.775	-.450	0.544	0.816	1.000							
	n	20.000	19.000	18.000	11.000	15.000	20.000	0.000							
	p	0.817	0.692	0.000	0.165	0.000	0.000	0.000							
Fe	R	0.113	-.054	-.205	0.000	0.023	-.011	-.030	1.000						
	n	10.000	10.000	9.000	0.000	10.000	10.000	10.000	0.000						
	p	0.756	0.883	0.598	0.000	0.950	0.976	0.934	0.000						
TDS	R	0.493	-.381	0.830	0.000	0.737	0.794	0.882	0.370	1.000					
	n	9.000	9.000	8.000	0.000	9.000	9.000	9.000	9.000	0.000					
	p	0.177	0.312	0.000	0.000	0.000	0.000	0.000	0.327	0.000					
TSS	R	0.453	-.098	-.160	0.127	0.055	0.061	0.115	0.602	0.359	1.000				
	n	19.000	18.000	17.000	10.000	15.000	19.000	19.000	10.000	9.000	0.000				
	p	0.050	0.699	0.540	0.726	0.845	0.806	0.640	0.066	0.343	0.000				
TOT.P	R	-.588	-.229	0.274	-.740	-.048	0.629	11.000	0.000	0.000	10.000	0.000			
	n	11.000	10.000	10.000	11.000	6.000	0.000	0.197	0.000	0.000	0.807	0.000			
	p	0.057	0.524	0.444	0.000	0.928	0.421	0.000	0.000	0.089	1.000	0.000			
TURB	R	0.392	-.665	0.625	0.000	0.776	0.437	0.452	0.866	0.226	0.000	1.000	1.000		
	n	10.000	10.000	9.000	0.000	10.000	10.000	10.000	9.000	10.000	0.000	0.000	0.000		
	p	0.262	0.000	0.070	0.000	0.000	0.207	0.190	0.000	0.530	0.000	0.000	0.000		
BOD	R	-.457	-.113	0.312	0.000	0.465	0.149	0.408	0.029	0.448	-.378	0.000	0.487	1.000	
	n	9.000	9.000	8.000	0.000	9.000	9.000	9.000	9.000	8.000	9.000	0.000	9.000	0.000	
	p	0.216	0.773	0.451	0.000	0.208	0.702	0.276	0.941	0.265	0.316	0.000	0.183	0.000	
Mn	R	0.491	-.915	0.636	0.000	0.888	0.217	0.252	0.070	0.615	0.073	0.000	0.775	0.143	1.000
	n	9.000	9.000	8.000	0.000	9.000	9.000	9.000	9.000	9.000	9.000	0.000	9.000	8.000	0.000
	p	0.179	0.000	0.090	0.000	0.000	0.575	0.514	0.858	0.078	0.853	0.000	0.014	0.735	0.000

APPENDIX 2-B.1 Outflow of Wainwright Dam.

		TEMP	Ph	COND	CHL-A	Cl	SO_4	Na	Fe	TDS	TSS	TOT.P	TURB	BOD	Mn
TEMP	R	1.000													
	n	0.000													
	p	0.000													
pH	R	-.244	1.000												
	n	25.000	0.000												
	p	0.239	0.000												
COND	R	0.406	0.043	1.000											
	n	30.000	25.000	0.000											
	p	0.000	0.840	0.000											
CHL-A	R	0.755	-.404	-.022	1.000										
	n	12.000	10.000	10.000	0.000										
	p	0.000	0.247	0.953	0.000										
Cl	R	0.093	-.704	0.501	-.227	1.000									
	n	15.000	15.000	14.000	6.000	0.000									
	p	0.741	0.000	0.060	0.665	0.000									
SO_4	R	0.137	0.371	0.867	-.530	0.228	1.000								
	n	20.000	19.000	19.000	11.000	15.000	0.000								
	p	0.565	0.118	0.000	0.094	0.413	0.000								
Na	R	0.227	-.038	0.898	-.445	0.494	0.868	1.000							
	n	19.000	18.000	18.000	10.000	14.000	19.000	0.000							
	p	0.350	0.882	0.000	0.198	0.072	0.000	0.000							
Fe	R	0.420	0.142	0.495	0.000	0.204	0.550	0.696	1.000						
	n	10.000	10.000	10.000	0.000	10.000	10.000	9.000	0.000						
	p	0.227	0.695	0.146	0.000	0.572	0.099	0.037	0.000						
TDS	R	0.586	-.011	0.880	0.000	0.665	0.813	0.919	0.658	0.000					
	n	9.000	9.000	9.000	0.000	9.000	9.000	9.000	1.000	0.000					
	p	0.098	0.977	0.000	0.000	0.050	0.000	0.000	0.000	0.000					
TSS	R	0.322	-.074	0.759	0.018	0.508	0.752	0.771	0.413	0.906	1.000				
	n	19.000	18.000	18.000	10.000	15.000	19.000	18.000	10.000	9.000	0.000				
	p	0.178	0.771	0.000	0.960	0.050	0.000	0.000	0.236	0.000	0.000				
TOT.P	R	0.769	0.289	0.457	-.826	0.542	0.824	0.621	0.000	0.000	0.306	1.000			
	n	11.000	10.000	10.000	11.000	6.000	11.000	10.000	0.000	0.000	10.000	0.000			
	p	0.000	0.418	0.185	0.000	0.266	0.000	0.055	0.000	0.000	0.389	0.000			
TURB	R	0.329	-.552	0.494	0.000	0.810	0.336	0.570	0.287	0.774	0.747	0.000	1.000		
	n	10.000	10.000	10.000	0.000	10.000	10.000	9.000	10.000	9.000	10.000	0.000	0.000		
	p	0.353	0.098	0.147	0.000	0.000	0.343	0.109	0.422	0.014	0.000	0.000	0.000		
BOD	R	-.539	0.111	-.314	0.000	-.163	-.264	-2.93	-.013	-.410	-.473	0.000	-.428	1.000	
	n	9.000	9.000	9.000	0.000	9.000	9.000	8.000	9.000	8.000	9.000	0.000	9.000	0.000	
	p	0.135	0.777	0.410	0.000	0.675	0.493	0.481	0.973	0.313	0.199	0.000	0.251	0.000	
Mn	R	0.414	-.694	0.452	0.000	0.965	0.147	0.440	0.367	0.675	0.465	0.000	0.866	-.406	1.000
	n	9.000	9.000	9.000	0.000	9.000	9.000	9.000	9.000	9.000	9.000	0.000	9.000	8.000	0.000
	p	0.267	0.038	0.220	0.000	0.000	0.707	0.236	0.331	0.050	0.208	0.000	0.000	0.318	0.000

APPENDIX 2-B.1 Minnitaki.

		TEMP	Ph	COND	CHL-A	Cl	SO_4	Na	Fe	TDS	TSS	TOT.P	TURB	BOD	Mn
TEMP	R	1.000													
	n	0.000													
	p	0.000													
pH	R	-.273	1.000												
	n	25.000	0.000												
	p	0.186	0.000												
COND	R	0.166	-.119	1.000											
	n	31.000	25.000	0.000											
	p	0.372	0.571	0.000											
CHL-A	R	0.994	-.735	-.562	1.000										
	n	3.000	3.000	3.000	0.000										
	p	0.069	0.474	0.620	0.000										
Cl	R	0.338	-.331	0.736	1.000	1.000									
	n	12.000	12.000	12.000	2.000	0.000									
	p	0.282	0.294	0.000	0.000	0.000									
SO_4	R	0.290	-.149	0.560	-.283	0.444	1.000								
	n	13.000	13.000	13.000	3.000	12.000	0.000								
	p	0.337	0.628	0.050	0.817	0.148	0.000								
Na	R	0.034	-.071	0.872	-.185	0.549	0.521	1.000							
	n	13.000	13.000	13.000	3.000	12.000	13.000	0.000							
	p	0.912	0.818	0.000	0.881	0.065	0.068	0.000							
Fe	R	0.408	-.295	0.730	0.000	0.742	0.477	0.517	1.000						
	n	11.000	11.000	11.000	0.000	11.000	11.000	11.000	0.000						
	p	0.213	0.379	0.000	0.000	0.000	0.138	103.000	0.000						
TDS	R	0.503	-.194	0.901	0.000	0.645	0.140	-.024	11.000	1.000					
	n	10.000	10.000	10.000	0.000	10.000	12.000	12.000	10.000	0.000					
	p	0.138	0.591	0.000	0.000	0.000	0.664	0.940	0.040	0.000					
TSS	R	0.382	0.245	0.079	1.000	0.140	-.024	0.031	0.697	0.780	1.000				
	n	12.000	12.000	12.000	0.000	12.000	12.000	12.000	11.000	10.000	0.000				
	p	0.221	0.442	0.807	0.000	0.664	0.940	0.925	0.000	0.000	0.000				
TOT.P	R	0.812	-1.000	0.133	0.744	1.000	0.430	0.518	0.000	0.000	-1.000	1.000			
	n	3.000	3.000	3.000	3.000	0.000	3.000	3.000	1.000	0.000	2.000	0.000			
	p	0.397	0.000	0.915	0.466	0.000	0.717	0.653	0.000	0.000	0.000	0.000			
TURB	R	0.224	-.080	0.906	0.000	0.619	0.442	0.875	0.675	0.813	0.769	0.000	1.000		
	n	11.000	11.000	11.000	1.000	11.000	11.000	11.000	11.000	10.000	11.000	1.000	0.000		
	p	0.504	0.815	0.000	0.000	0.173	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
BOD	R	-.149	0.212	0.676	1.000	0.155	0.440	0.884	0.378	0.714	0.389	0.000	0.724	1.000	
	n	10.000	10.000	10.000	1.000	10.000	10.000	10.000	10.000	9.000	10.000	1.000	10.000	0.000	
	p	0.682	0.556	0.032	0.000	0.670	0.203	0.000	0.281	0.000	0.267	0.000	0.000	0.000	
Mn	R	0.585	-.172	0.926	0.000	0.792	0.699	0.828	0.745	0.887	0.890	0.000	0.881	0.605	1.000
	n	10.000	10.000	10.000	0.000	10.000	10.000	10.000	10.000	10.000	10.000	0.000	10.000	9.000	0.000
	p	0.076	0.635	0.000	0.000	0.000	0.000	0.000	0.013	0.000	0.000	0.000	0.000	0.084	0.000

APPENDIX 2-B.1 Clay Lake inflow.

		TEMP	Ph	COND	CHL-A	Cl	SO_4	Na	Fe	TDS	TSS	TOT.P	TURB	BOD	Mn
TEMP	R	1.000													
	n	0.000													
	p	0.000													
pH	R	0.410	1.000												
	n	26.000	0.000												
	p	0.000	0.000												
COND	R	-.560	-.292	1.000											
	n	30.000	24.000	0.000											
	p	0.000	0.167	0.000											
CHL-A	R	0.371	0.069	-.230	1.000										
	n	15.000	15.000	13.000	0.000										
	p	0.173	0.807	0.450	0.000										
Cl	R	-.349	0.139	0.462	0.028	1.000									
	n	13.000	12.000	11.000	8.000	0.000									
	p	0.242	0.666	0.152	0.948	0.000									
SO_4	R	-.267	0.115	0.551	-.163	0.614	1.000								
	n	26.000	25.000	23.000	16.000	14.000	0.000								
	p	0.187	0.583	0.000	0.546	0.000	0.000								
Na	R	-.536	-.390	0.705	0.070	0.830	0.534	1.000							
	n	25.000	24.000	22.000	15.000	14.000	26.000	0.000							
	p	0.000	0.060	0.000	0.805	0.000	0.000	0.000							
Fe	R	0.078	-.595	-.444	0.852	0.028	-.380	0.389	1.000						
	n	13.000	12.000	11.000	8.000	14.000	14.000	14.000	0.000						
	p	0.799	0.000	0.171	0.000	0.925	0.180	0.169	0.000						
TDS	R	-.132	0.280	-.484	0.000	0.304	-.438	-.137	-.482	1.000					
	n	7.000	6.000	6.000	1.000	7.000	7.000	7.000	7.000	0.000					
	p	0.778	0.591	0.331	0.000	0.508	0.326	0.770	0.273	0.000					
TSS	R	0.247	0.038	-.235	0.372	-.712	-.202	-.163	0.078	-.256	1.000				
	n	23.000	22.000	20.000	13.000	13.000	24.000	24.000	13.000	7.000	0.000				
	p	0.256	0.865	0.320	0.210	0.000	0.343	0.448	0.800	0.580	0.000				
TOT.P	R	0.839	0.173	-.510	0.833	-.390	-.392	-.331	-.149	0.000	0.334	1.000			
	n	17.000	17.000	15.000	13.000	7.000	18.000	18.000	7.000	0.000	17.000	0.000			
	p	0.000	0.506	0.050	0.000	0.387	0.107	0.179	0.749	0.000	0.191	0.000			
TURB	R	0.391	0.128	0.263	1.000	0.375	0.367	0.300	0.455	-.220	0.136	0.000	1.000		
	n	8.000	7.000	7.000	2.000	8.000	8.000	8.000	8.000	7.000	8.000	0.000	0.000		
	p	0.338	0.785	0.570	0.000	0.361	0.371	0.470	0.258	0.635	0.748	0.000	0.000		
BOD	R	-.434	-.213	0.512	1.000	0.015	0.179	0.304	0.161	-.384	-.229	0.000	-.410	1.000	
	n	8.000	7.000	7.000	2.000	8.000	8.000	8.000	8.000	7.000	8.000	0.000	8.000	0.000	
	p	0.280	0.647	0.240	0.000	0.972	0.672	0.463	0.703	0.395	0.585	0.000	0.313	0.000	
Mn	R	0.328	-.205	0.681	0.000	0.420	0.607	0.607	0.705	-.589	-.304	0.000	0.551	0.303	1.000
	n	7.000	6.000	6.000	0.000	7.000	7.000	7.000	7.000	7.000	7.000	0.000	7.000	7.000	0.000
	p	0.472	0.697	0.136	0.000	0.348	0.149	0.150	0.077	0.164	0.506	0.000	0.200	0.509	0.000

APPENDIX 2-B.1 Clay Lake, eastern basin.

		TEMP	Ph	COND	CHL-A	Cl	SO_4	Na	Fe	TDS	TSS	TOT.P	TURB	BOD	Mn
TEMP	R	1.000													
	n	0.000													
	p	0.000													
pH	R	0.410	1.000												
	n	26.000	0.000												
	p	0.000	0.000												
COND	R	-.560	-.292	1.000											
	n	30.000	24.000	0.000											
	p	0.000	0.167	0.000											
CHL-A	R	0.371	0.069	-.230	1.000										
	n	15.000	15.000	13.000	0.000										
	p	0.173	0.807	0.450	0.000										
Cl	R	-.349	0.139	0.462	0.028	1.000									
	n	13.000	12.000	11.000	8.000	0.000									
	p	0.242	0.666	0.152	0.948	0.000									
SO_4	R	-.267	0.115	0.551	-.163	0.614	1.000								
	n	26.000	25.000	23.000	16.000	14.000	0.000								
	p	0.187	0.583	0.000	0.546	0.000	0.000								
Na	R	-.536	-.390	0.705	0.070	0.830	0.534	1.000							
	n	25.000	24.000	22.000	15.000	14.000	26.000	0.000							
	p	0.000	0.060	0.000	0.805	0.000	0.000	0.000							
Fe	R	0.078	-.595	-.444	0.852	0.028	-.380	0.389	1.000						
	n	13.000	12.000	11.000	8.000	14.000	14.000	14.000	0.000						
	p	0.799	0.000	0.171	0.000	0.925	0.180	0.169	0.000						
TDS	R	-.132	0.280	-.484	0.000	0.304	-.438	-.137	-.482	1.000					
	n	7.000	6.000	6.000	1.000	7.000	7.000	7.000	7.000	0.000					
	p	0.778	0.591	0.331	0.000	0.508	0.326	0.770	0.273	0.000					
TSS	R	0.247	0.038	-.235	0.372	-.712	-.202	-.163	0.078	-.256	1.000				
	n	23.000	22.000	20.000	13.000	13.000	24.000	24.000	13.000	7.000	0.000				
	p	0.256	0.865	0.320	0.210	0.000	0.343	0.448	0.800	0.580	0.000				
TOT.P	R	0.839	0.173	-.510	0.833	-.390	-.392	-.331	-.149	0.000	0.334	1.000			
	n	17.000	17.000	15.000	13.000	7.000	18.000	18.000	7.000	0.000	17.000	0.000			
	p	0.000	0.506	0.050	0.000	0.387	0.107	0.179	0.749	0.000	0.191	0.000			
TURB	R	0.391	0.128	0.263	1.000	0.375	0.367	0.300	0.455	-.220	0.136	0.000	1.000		
	n	8.000	7.000	7.000	2.000	8.000	8.000	8.000	8.000	7.000	8.000	0.000	0.000		
	p	0.338	0.785	0.570	0.000	0.361	0.371	0.470	0.258	0.635	0.748	0.000	0.000		
BOD	R	-.434	-.213	0.512	1.000	0.015	0.179	0.304	0.161	-.384	-.229	0.000	-.410	1.000	
	n	8.000	7.000	7.000	2.000	8.000	8.000	8.000	8.000	7.000	8.000	0.000	8.000	0.000	
	p	0.280	0.647	0.240	0.000	0.972	0.672	0.463	0.703	0.395	0.585	0.000	0.313	0.000	
Mn	R	0.328	-.205	0.681	0.000	0.420	0.607	0.607	0.705	-.589	-.304	0.000	0.551	0.303	1.000
	n	7.000	6.000	6.000	0.000	7.000	7.000	7.000	7.000	7.000	7.000	0.000	7.000	7.000	0.000
	p	0.472	0.697	0.136	0.000	0.348	0.149	0.150	0.077	0.164	0.506	0.000	0.200	0.509	0.000

APPENDIX 2-B.1 Clay Lake, western basin epilimnion.

		TEMP	Ph	COND	CHL-A	Cl	SO_4	Na	Fe	TDS	TSS	TOT.P	TURB	BOD	Mn
TEMP	R	1.000													
	n	0.000													
	p	0.000													
pH	R	0.557	1.000												
	n	28.000	0.000												
	p	0.000	0.000												
COND	R	-.515	-.478	1.000											
	n	31.000	27.000	0.000											
	p	0.000	0.000	0.000											
CHL-A	R	0.304	0.206	-.082	1.000										
	n	16.000	16.000	15.000	0.000										
	p	0.252	0.443	0.770	0.000										
Cl	R	-.674	-.624	0.992	0.000	1.000									
	n	8.000	8.000	8.000	0.000	0.000									
	p	0.067	0.098	0.000	0.000	0.000									
SO_4	R	-.430	-.298	0.596	0.070	0.738	1.000								
	n	28.000	28.000	27.000	16.000	8.000	0.000								
	p	0.000	0.123	0.000	0.797	0.000	0.000								
Na	R	-.617	-.506	0.804	-.391	0.866	0.476	1.000							
	n	26.000	26.000	25.000	14.000	8.000	26.000	0.000							
	p	0.000	0.000	0.000	0.166	0.000	0.000	0.000							
Fe	R	-.778	-.292	0.622	0.000	0.632	0.514	0.885	1.000						
	n	8.000	8.000	8.000	0.000	8.000	8.000	8.000	0.000						
	p	0.023	0.484	0.100	0.000	0.093	0.192	0.000	0.000						
TDS	R	-.423	-.476	0.518	0.000	0.537	0.157	0.297	0.321	1.000					
	n	8.000	8.000	8.000	0.000	8.000	8.000	8.000	8.000	0.000					
	p	0.296	0.233	0.188	0.000	0.170	0.711	0.476	0.439	0.000					
TSS	R	-.812	-.284	0.316	-.242	0.557	0.169	0.442	0.581	0.233	1.000				
	n	25.000	25.000	24.000	13.000	8.000	25.000	24.000	8.000	8.000	0.000				
	p	0.000	0.168	0.133	0.425	0.151	0.420	0.000	0.131	0.578	0.000				
TOT.P	R	-.206	-.578	-.119	-.134	0.000	-.164	-.160	0.000	0.000	0.065	1.000			
	n	19.000	19.000	18.000	14.000	1.000	19.000	18.000	0.000	0.000	18.000	0.000			
	p	0.397	0.000	0.639	0.648	0.000	0.503	0.525	0.000	0.000	0.797	0.000			
TURB	R	-.902	-.730	0.824	-1.000	0.805	0.444	0.866	0.792	0.329	0.851	-1.000	1.000		
	n	9.000	9.000	9.000	2.000	8.000	9.000	9.000	8.000	8.000	9.000	2.000	0.000		
	p	0.000	0.000	0.000	0.000	0.000	0.231	0.000	0.000	0.427	0.000	0.000	0.000		
BOD	R	-.649	-.799	0.856	-1.000	0.844	0.451	0.697	0.453	0.584	0.578	-1.000	0.790	1.000	
	n	9.000	9.000	9.000	2.000	8.000	9.000	9.000	8.000	8.000	9.000	2.000	9.000	0.000	
	p	0.059	0.000	0.000	0.000	0.000	0.223	0.000	0.260	0.129	0.103	0.000	0.000	0.000	
Mn	R	-.446	0.066	-.043	0.000	-.018	-.191	0.066	0.278	0.052	0.310	0.000	0.339	-.044	1.000
	n	8.000	8.000	8.000	0.000	8.000	8.000	8.000	8.000	8.000	8.000	0.000	8.000	8.000	0.000
	p	0.268	0.877	0.920	0.000	0.966	0.650	0.878	0.505	0.902	0.455	0.000	0.412	0.918	0.000

APPENDIX 2-B.1 Clay Lake outflow.

		TEMP	Ph	COND	CHL-A	Cl	SO_4	Na	Fe	TDS	TSS	TOT.P	TURB	BOD	Mn
TEMP	R	1.000													
	n	0.000													
	p	0.000													
pH	R	0.771	1.000												
	n	23.000	0.000												
	p	0.000	0.000												
COND	R	-.614	-.724	1.000											
	n	26.000	26.000	0.000											
	p	0.000	0.000	0.000											
CHL-A	R	0.745	0.387	-.258	1.000										
	n	14.000	16.000	14.000	0.000										
	p	0.000	0.139	0.374	0.000										
Cl	R	-.266	-.093	-.403	0.103	1.000									
	n	7.000	11.000	11.000	4.000	0.000									
	p	0.565	0.786	0.219	0.897	0.000									
SO_4	R	-.655	-.419	0.716	-.550	-.550	1.000								
	n	22.000	26.000	24.000	14.000	10.000	0.000								
	p	0.000	0.000	0.000	0.000	0.099	0.000								
Na	R	-.762	-.696	0.803	-.494	0.295	0.622	1.000							
	n	23.000	27.000	25.000	15.000	11.000	26.000	0.000							
	p	0.000	0.000	0.000	0.061	0.379	0.000	0.000							
Fe	R	-.809	-.725	0.550	-1.000	0.576	0.583	0.555	1.000						
	n	5.000	9.000	9.000	2.000	9.000	9.000	9.000	0.000						
	p	0.097	0.000	0.125	0.000	0.104	0.100	0.121	0.000						
TDS	R	-.360	-.411	0.304	0.000	0.232	0.176	0.198	0.501	1.000					
	n	4.000	8.000	8.000	0.000	8.000	8.000	8.000	8.000	0.000					
	p	0.640	0.312	0.464	0.000	0.581	0.676	0.637	0.206	0.000					
TSS	R	-.685	-.456	0.336	-.148	0.266	0.277	0.292	0.937	0.502	1.000				
	n	21.000	25.000	23.000	13.000	10.000	25.000	25.000	9.000	8.000	0.000				
	p	0.000	0.000	0.117	0.630	0.457	0.180	0.156	0.000	0.205	0.000				
TOT.P	R	0.021	0.225	-.513	0.064	0.566	-.294	-.293	0.000	0.000	0.194	1.000			
	n	18.000	18.000	16.000	13.000	3.000	17.000	18.000	0.000	0.000	17.000	0.000			
	p	0.935	0.370	0.000	0.836	0.617	0.251	0.239	0.000	0.000	0.456	0.000			
TURB	R	-.906	-.694	0.846	-1.000	0.855	0.685	0.908	0.728	0.498	0.696	0.000	1.000		
	n	5.000	9.000	9.000	2.000	9.000	9.000	9.000	9.000	8.000	9.000	0.000	0.000		
	p	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.209	0.000	0.000	0.000		
BOD	R	-.786	-.676	0.865	-1.000	0.848	0.282	0.700	0.628	0.136	0.685	0.000	0.652	1.000	
	n	5.000	9.000	9.000	0.000	9.000	9.000	9.000	9.000	8.000	9.000	0.000	9.000	0.000	
	p	0.115	0.050	0.000	0.000	0.000	0.463	0.000	0.070	0.747	0.000	0.000	0.057	0.000	
Mn	R	-.775	0.036	0.330	0.000	0.392	0.261	0.578	0.275	0.392	0.150	0.000	0.651	0.217	1.000
	n	4.000	8.000	8.000	0.000	8.000	8.000	8.000	8.000	8.000	8.000	0.000	8.000	8.000	0.000
	p	0.225	0.932	0.425	0.000	0.337	0.531	0.134	0.509	0.337	0.723	0.000	0.081	0.606	0.000

APPENDIX 2-B.1 Inflow to Ball Lake.

		TEMP	Ph	COND	CHL-A	Cl	SO_4	Na	Fe	TDS	TSS	TOT.P	TURB	BOD	Mn
TEMP	R	1.000													
	n	0.000													
	p	0.000													
pH	R	0.720	1.000												
	n	11.000	0.000												
	p	0.000	0.000												
COND	R	-.905	-.876	1.000											
	n	12.000	11.000	0.000											
	p	0.000	0.000	0.000											
CHL-A	R	0.000	0.000	0.000	1.000										
	n	0.000	0.000	0.000	0.000										
	p	0.000	0.000	0.000	0.000										
Cl	R	-.824	-.852	0.937	0.000	1.000									
	n	11.000	11.000	11.000	0.000	0.000									
	p	0.000	0.000	0.000	0.000	0.000									
SO_4	R	-.974	-.752	0.902	0.000	0.875	1.000								
	n	11.000	11.000	11.000	0.000	11.000	0.000								
	p	0.000	0.000	0.000	0.000	0.000	0.000								
Na	R	-.734	-.777	0.895	0.000	0.955	0.790	1.000							
	n	10.000	10.000	10.000	0.000	10.000	10.000	0.000							
	p	0.000	0.000	0.000	0.000	0.000	0.000	0.000							
Fe	R	-.006	-.270	0.090	0.000	0.163	0.057	0.316	1.000						
	n	11.000	11.000	11.000	0.000	11.000	11.000	10.000	0.000						
	p	0.986	0.422	0.772	0.000	0.631	0.867	0.374	0.000						
TDS	R	-.342	-.044	0.210	0.000	0.330	0.296	0.239	0.263	1.000					
	n	10.000	10.000	10.000	0.000	10.000	10.000	10.000	10.000	0.000					
	p	0.333	0.904	0.561	0.000	0.351	0.407	0.507	0.463	0.000					
TSS	R	0.260	0.010	-.178	0.000	-.317	-.206	-.248	0.082	-.803	1.000				
	n	10.000	10.000	10.000	0.000	10.000	10.000	10.000	10.000	10.000	0.000				
	p	0.468	0.784	0.624	0.000	0.372	0.569	0.490	0.822	0.000	0.000				
TOT.P	R	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000			
	n	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000			
	p	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000			
TURB	R	0.092	0.271	-.183	0.000	-.262	-.138	0.181	0.578	0.345	-.081	0.000	1.000		
	n	11.000	11.000	11.000	0.000	11.000	11.000	10.000	11.000	10.000	10.000	0.000	0.000		
	p	0.787	0.421	0.589	0.000	0.436	0.686	0.617	0.062	0.329	0.823	0.000	0.000		
BOD	R	-.285	-.394	0.444	0.000	0.444	0.232	0.474	-.480	-.231	-.116	0.000	-.570	1.000	
	n	11.000	11.000	11.000	0.000	11.000	11.000	10.000	11.000	10.000	10.000	0.000	11.000	0.000	
	p	0.395	0.231	0.171	0.000	0.171	0.493	0.166	0.135	0.520	0.749	0.000	0.067	0.000	
Mn	R	-.405	-.747	0.673	0.000	0.567	0.463	0.443	0.063	-.257	0.314	0.000	-.477	0.415	1.000
	n	10.000	10.000	10.000	0.000	10.000	10.000	10.000	10.000	10.000	10.000	0.000	10.000	10.000	0.000
	p	0.246	0.000	0.000	0.000	0.087	0.177	0.200	0.864	0.473	0.377	0.000	0.167	0.230	0.000

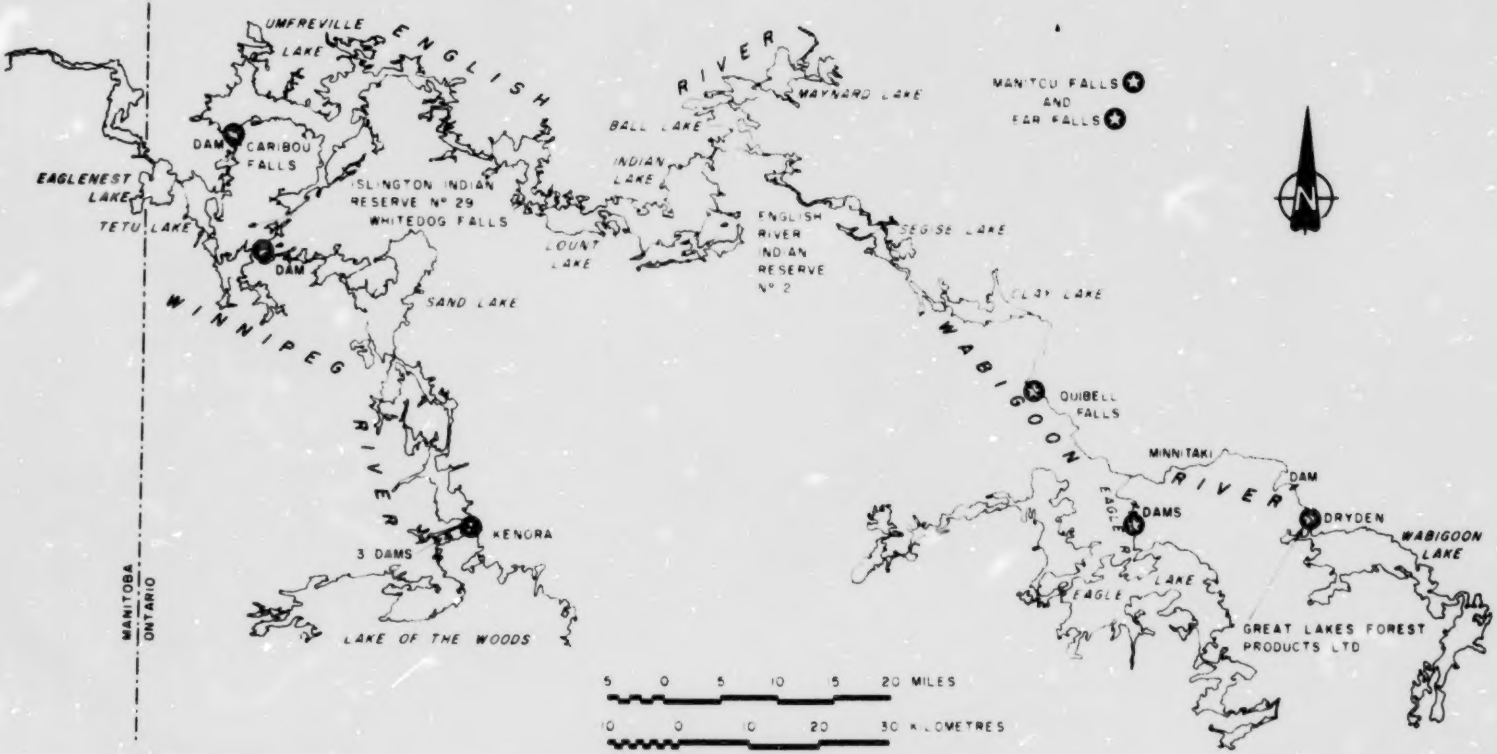
UMFREVILLE LAKE
ENGLISH
RIVER
MAYNARD LAKE
MANITOU FALLS AND FAR FALLS
DAM
CARIBOU FALLS
BALL LAKE
INDIAN LAKE
EAGLENEST LAKE
ISLINGTON INDIAN RESERVE Nº 29
WHITEDOG FALLS
TETU LAKE
DAM
LOUNT LAKE
ENGLISH RIVER INDIAN RESERVE Nº 2
SEGISE LAKE
SAND LAKE
CLAY LAKE
WINNIPEG
RIVER
WABIGOON
QUIBELL FALLS
MINNITAKI
RIVER
DAM
DRYDEN
WABIGOON LAKE
EAGLE
DAMS
EAGLE LAKE
KENORA
3 DAMS
MANITOBA
ONTARIO
LAKE OF THE WOODS
GREAT LAKES FOREST PRODUCTS LTD
5 0 5 10 15 20 MILES
10 0 10 20 30 KILOMETRES
N

Figure 2.1 Hydrometric stations and water sampling sites on the Wabigoon/English/Winnipeg River System.

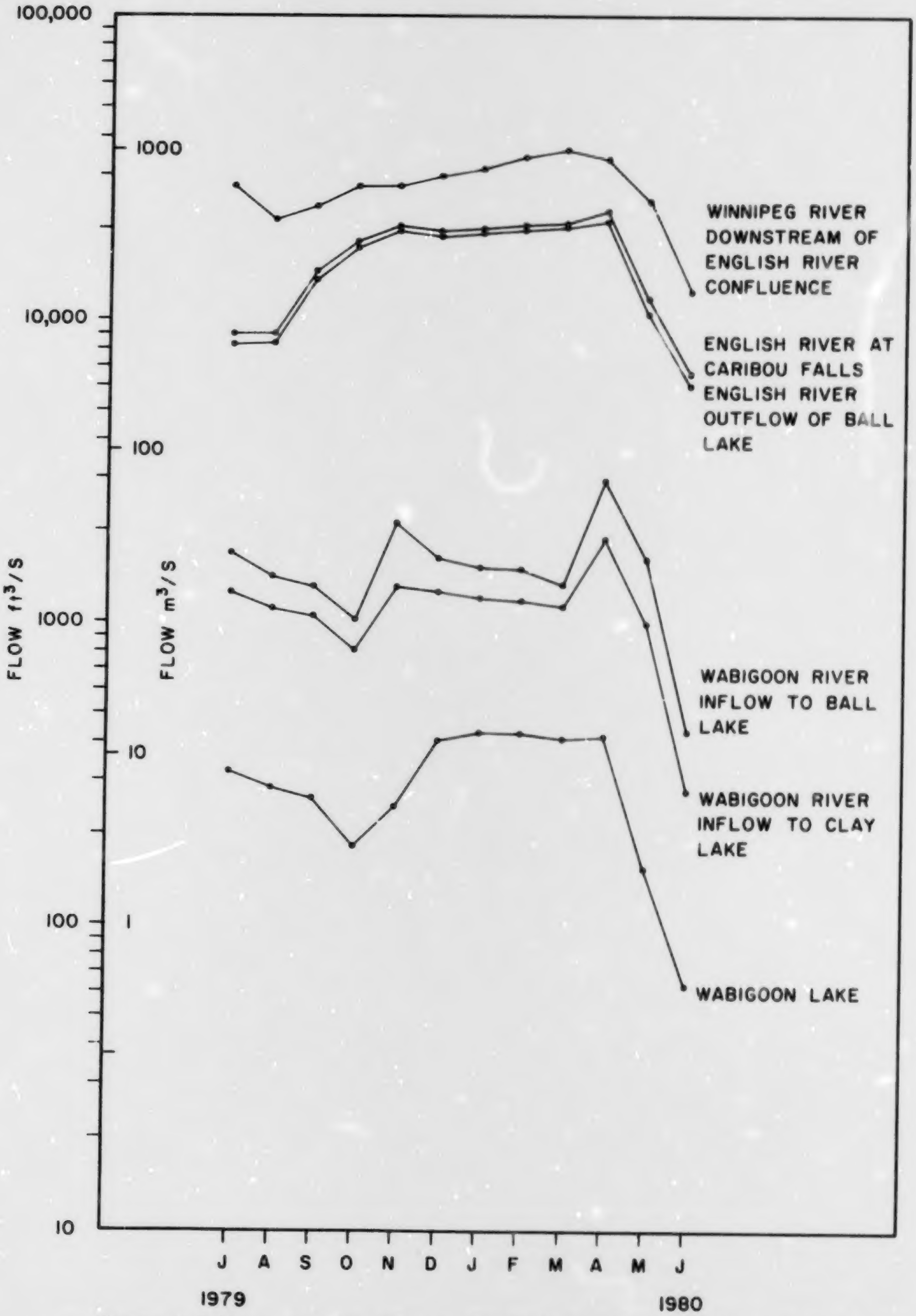

Figure 2.2 Mean monthly flows in the Wabigoon/English/Winnipeg River System, July, 1979-June, 1980.

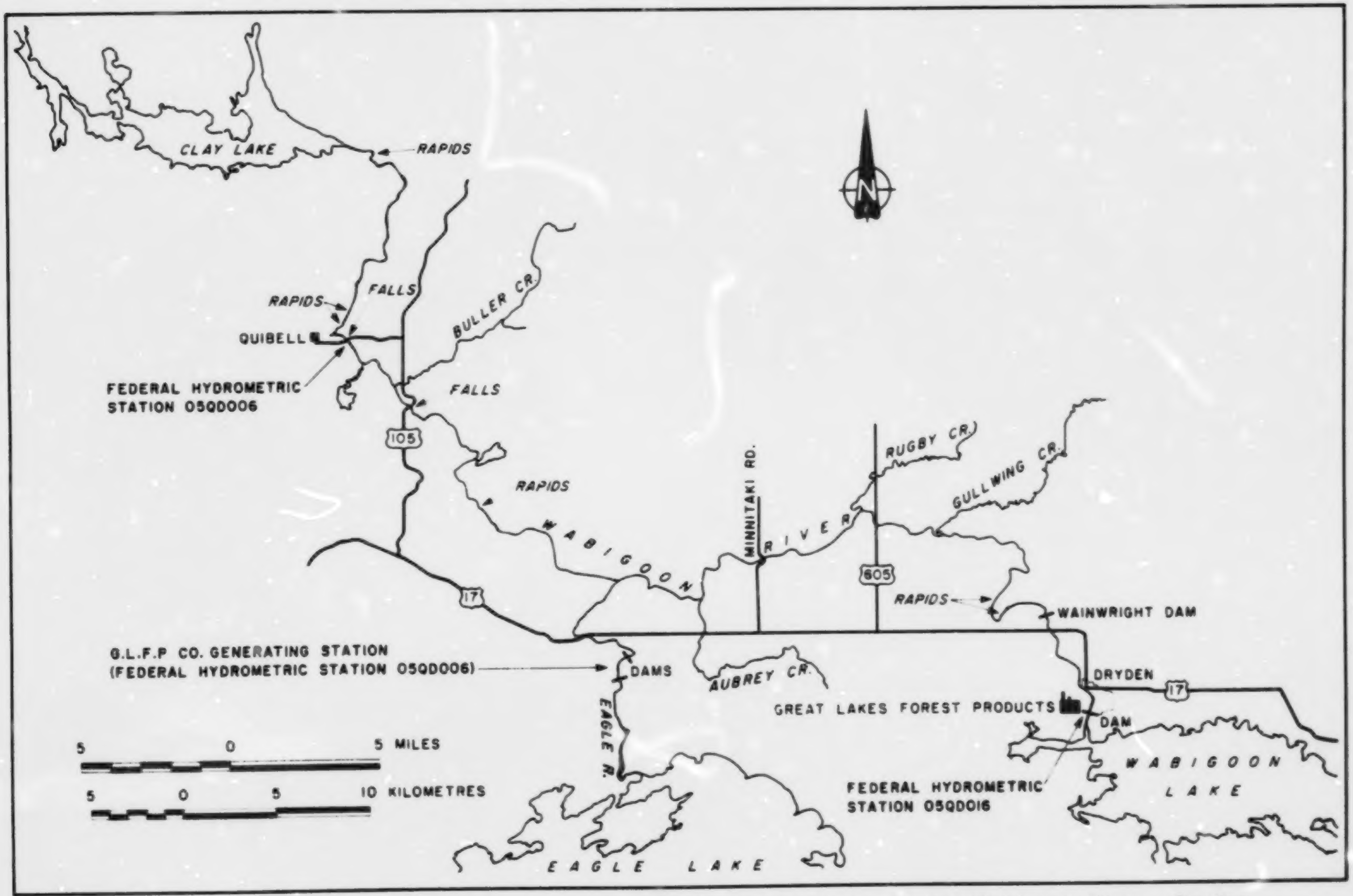
CLAY LAKE
RAPIDS
RAPIDS
FALLS
QUIBELL
FEDERAL HYDROMETRIC STATION 05QD006
BULLER CR.
FALLS
105
RAPIDS
W A B I G O O N
R I V E R
MINNITAKI RD.
RUGBY CR.
GULLWING CR.
605
RAPIDS
WAINWRIGHT DAM
17
G.L.F.P CO. GENERATING STATION (FEDERAL HYDROMETRIC STATION 05QD006)
DAMS
AUBREY CR.
DRYDEN
17
GREAT LAKES FOREST PRODUCTS
DAM
EAGLE R.
5 0 5 MILES
5 0 5 10 KILOMETRES
FEDERAL HYDROMETRIC STATION 05QD016
W A B I G O O N L A K E
E A G L E L A K E
N

Figure 2.3 Streamflow gauging stations and major morphological features of the Wabigoon River, Dryden to Clay Lake.

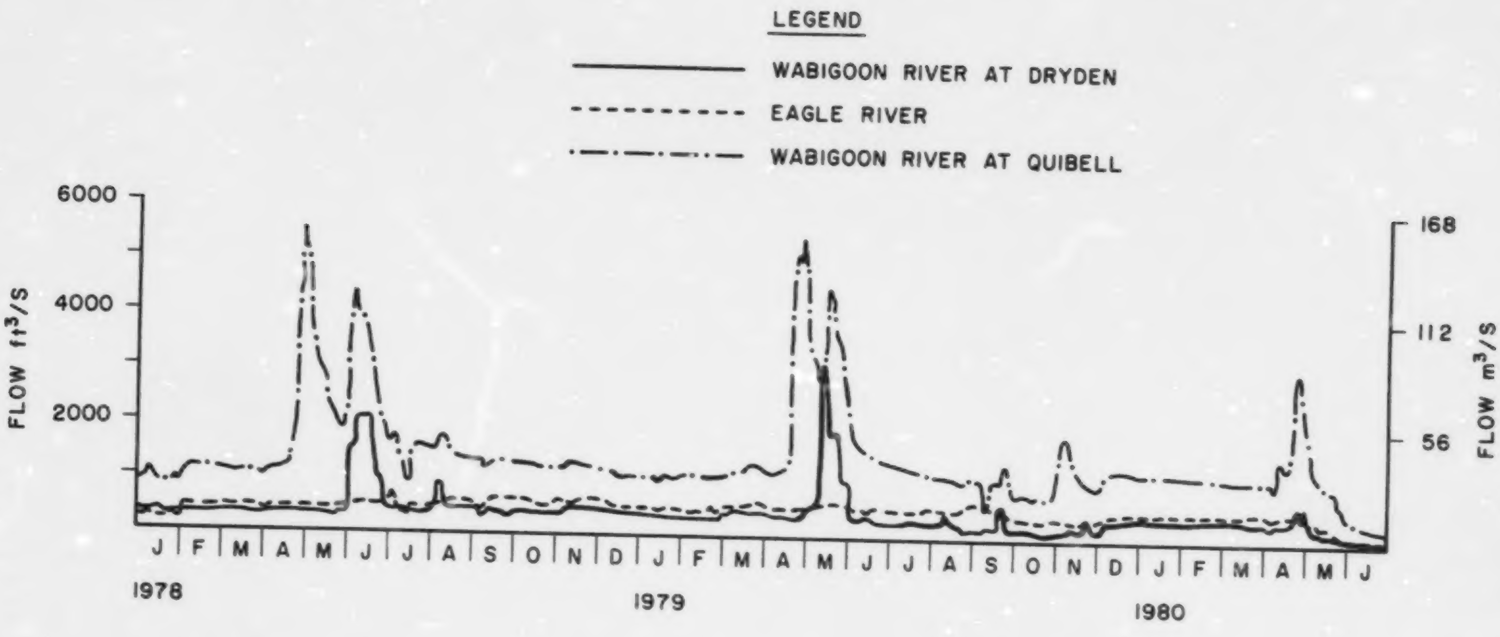

Figure 2.4 Hydrographs for three sites in the Wabigoon River Watershed, January, 1978–June, 1980.

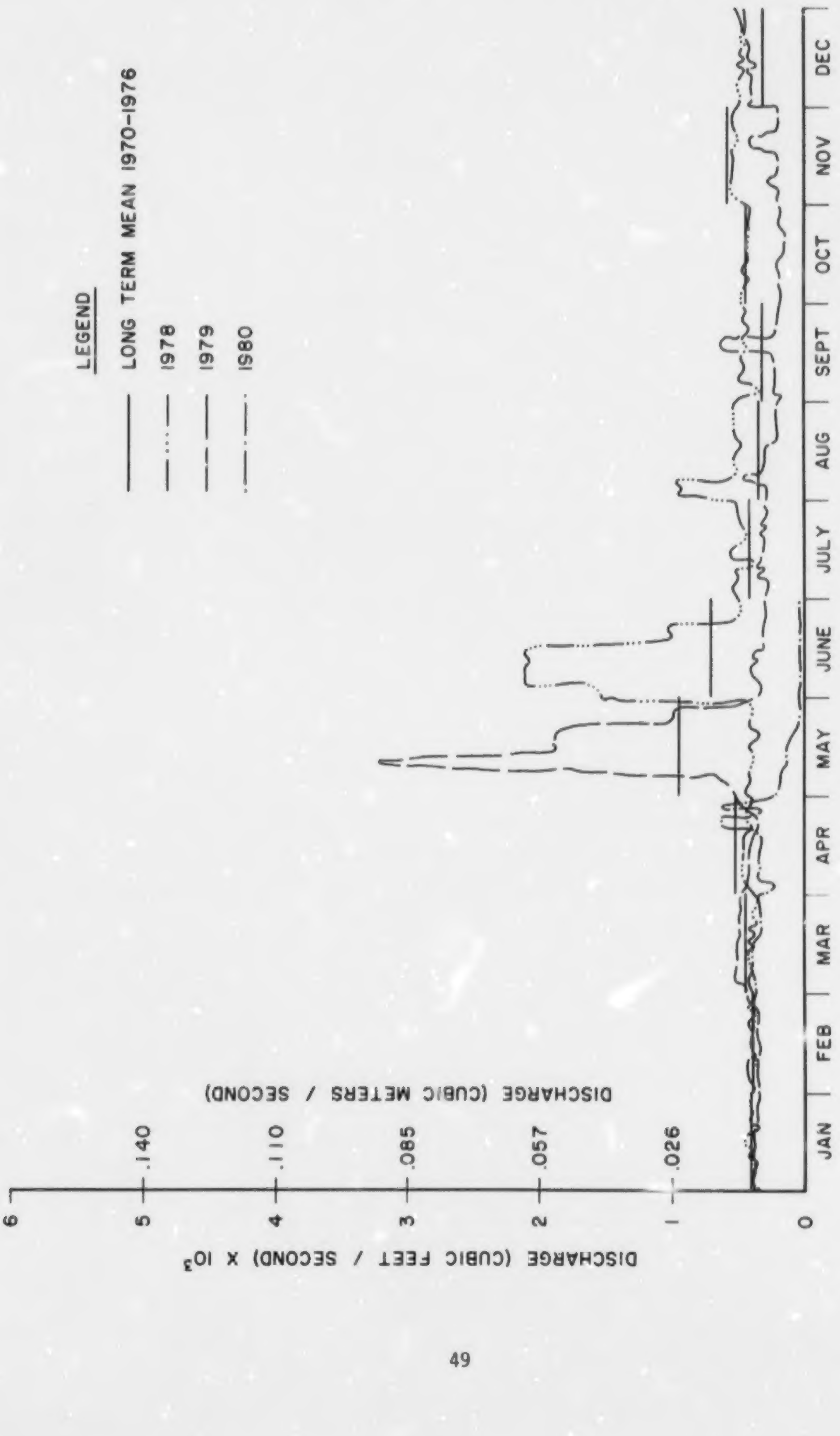

Figure 2.5 Hydrographs for study period and historical trends for the Wabigoon River at Dryden.

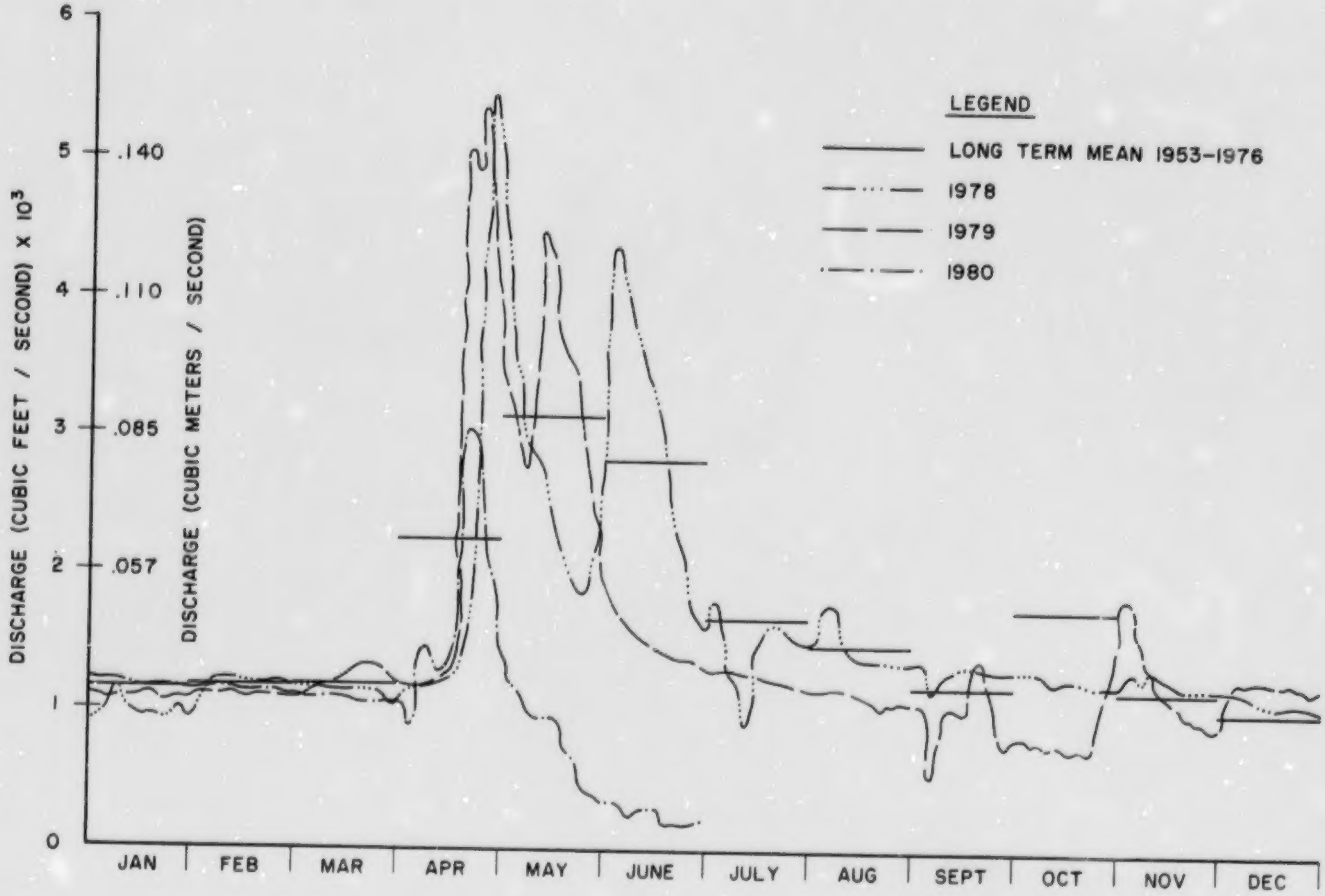

Figure 2.6 Hydrographs for study period and historical trends for the Wabigoon River at Quibell.

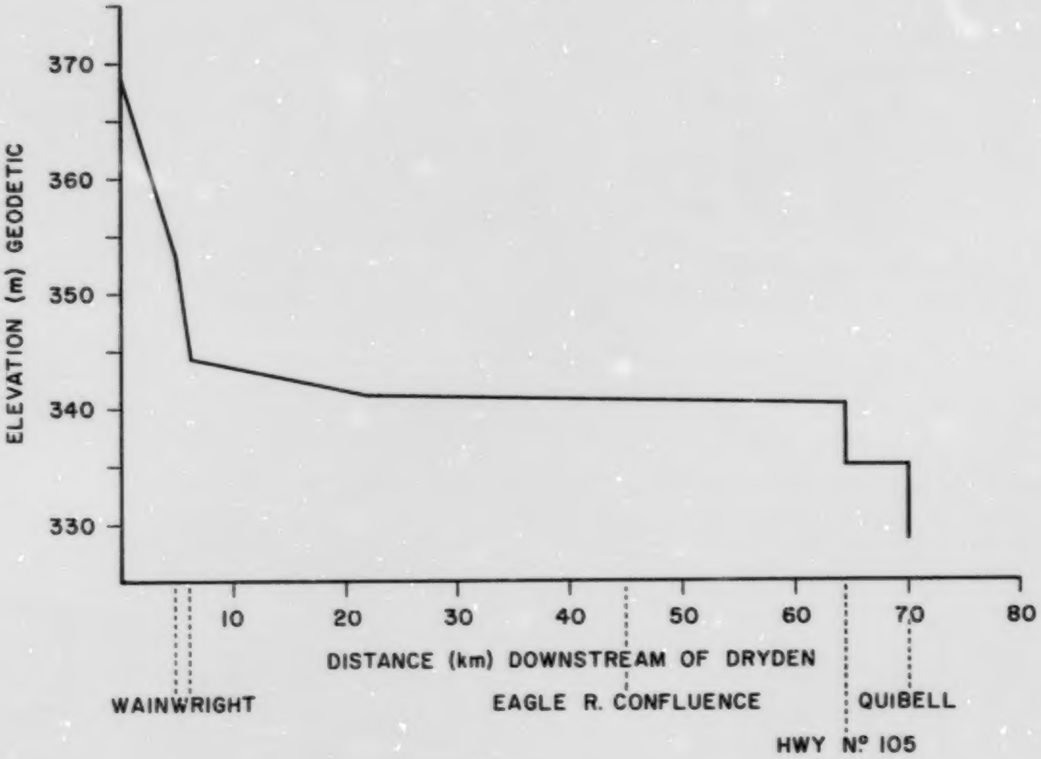

Figure 2.7 Water surface profile, Wabigoon River, October 1, 1980.

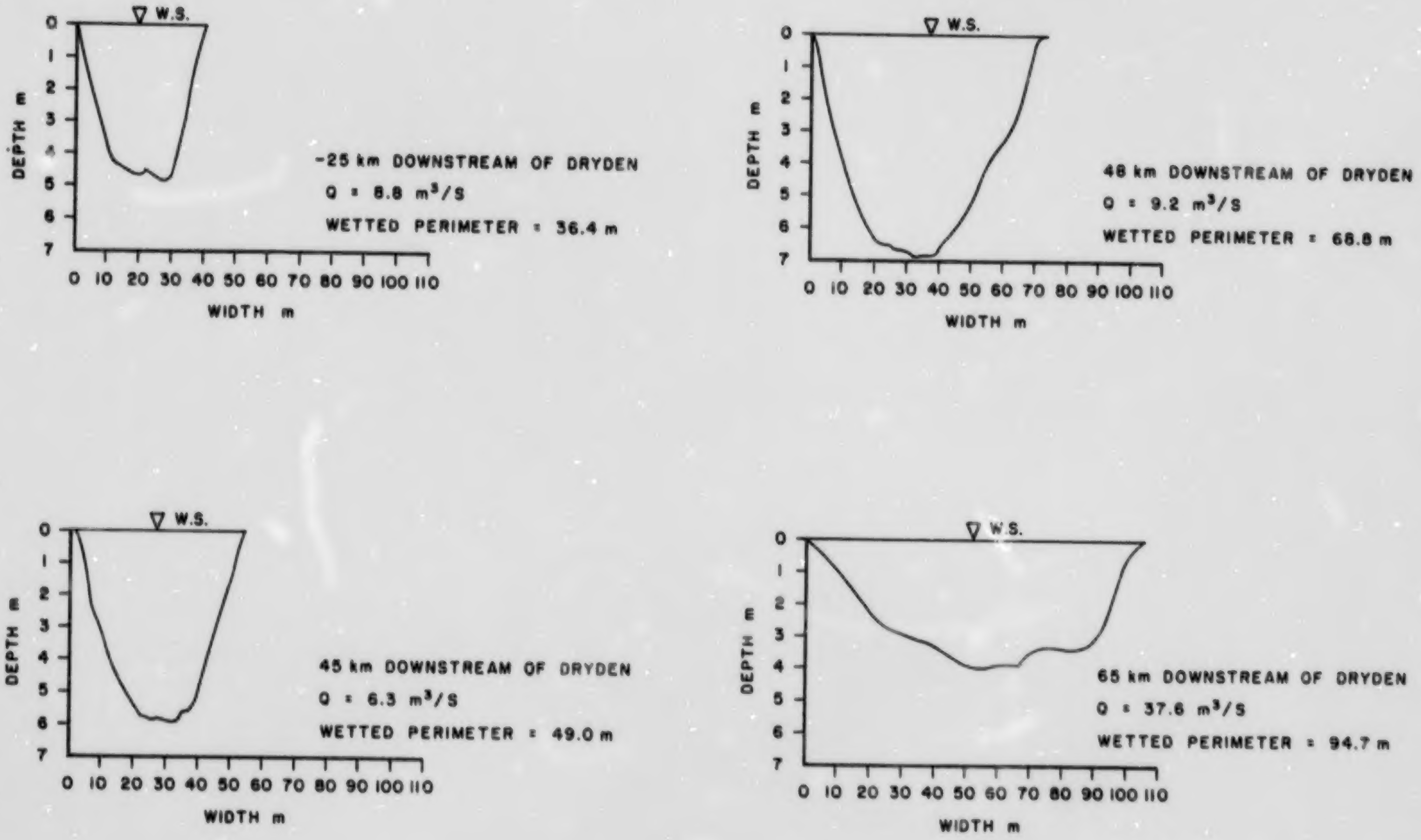

Figure 2.8 Channel cross sections for four typical sites in the Wabigoon River.

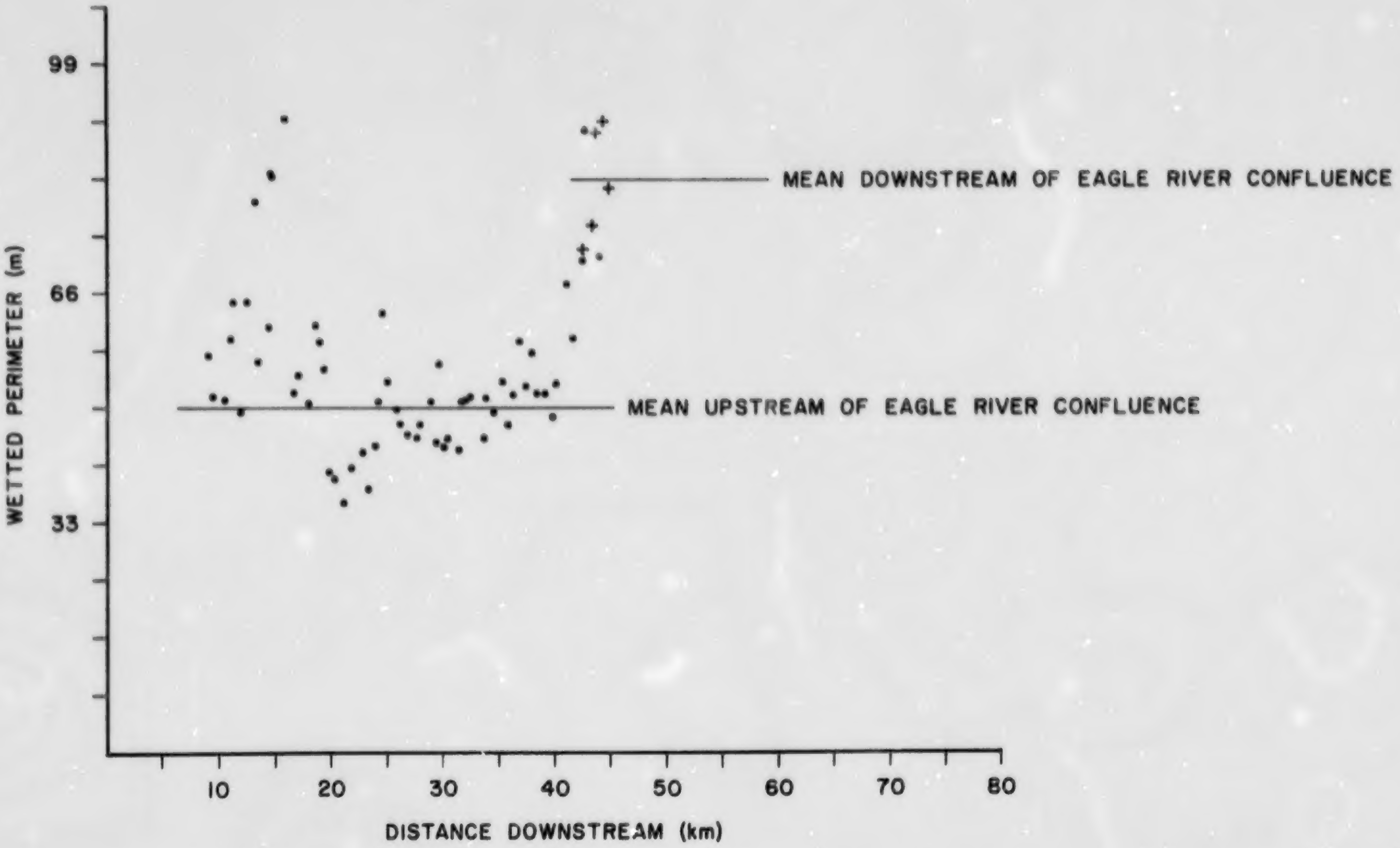

Figure 2.9 Wetted perimeter measurements of the Wabigoon River.

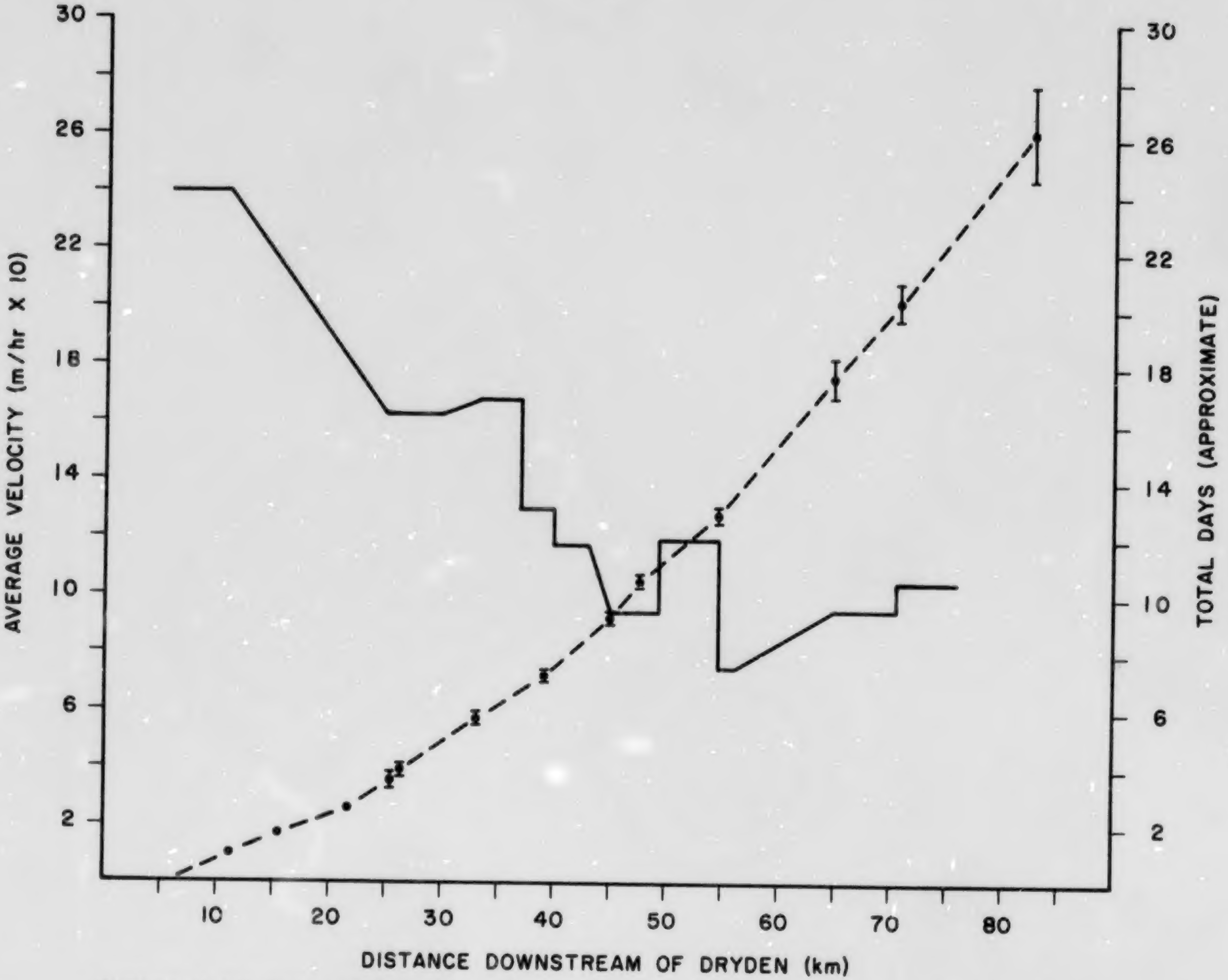

Figure 2.10 Time of travel and velocity measurements, Wabigoon River, Dryden to Clay Lake, August 4-10 1980.

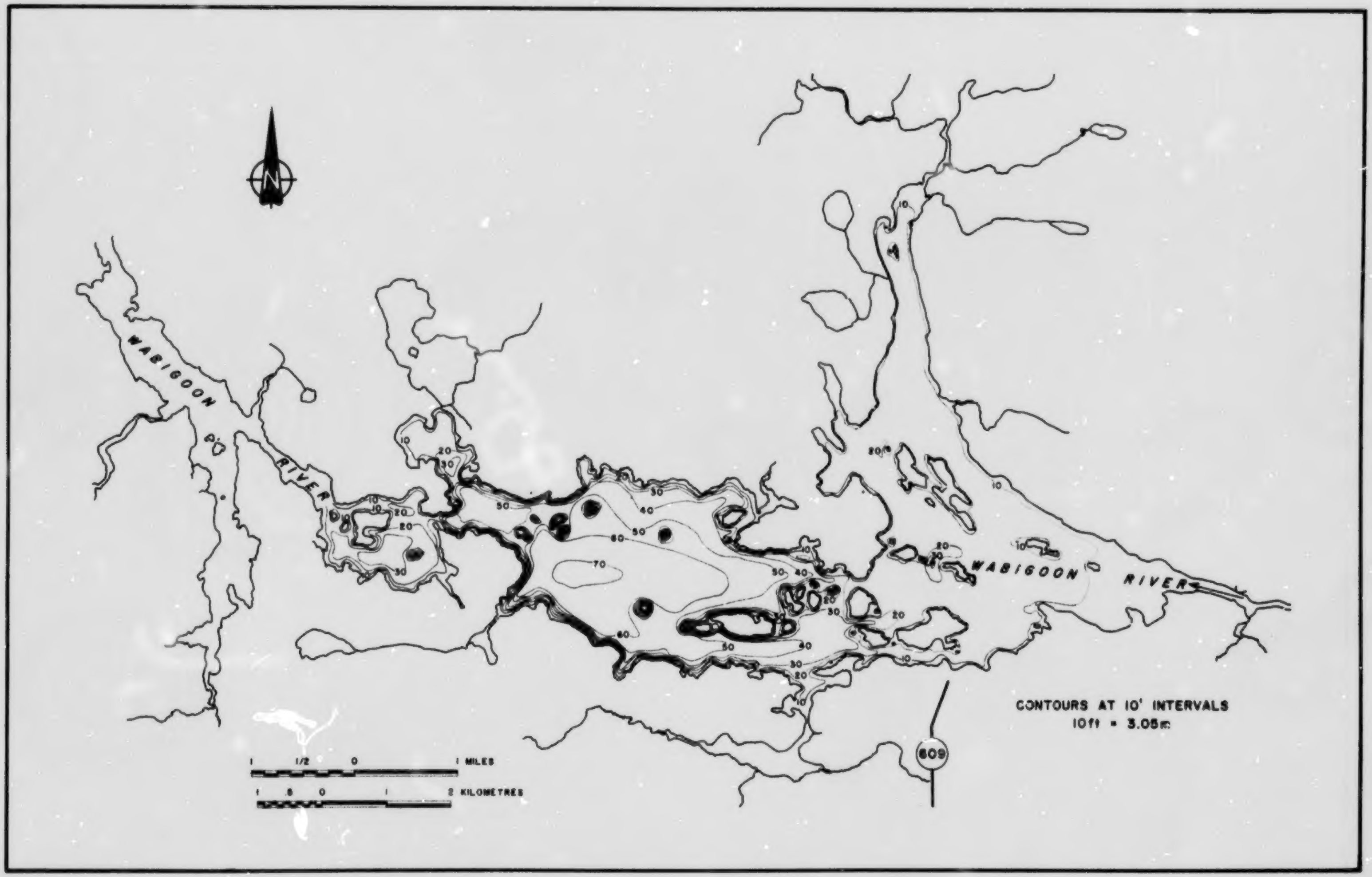
N
WABIGOON
RIVER
WABIGOON
RIVER
10
20
30
40
50
60
70
CONTOURS AT 10' INTERVALS
10ft = 3.05m
1 1/2 0 1 MILES
1 .5 0 1 2 KILOMETRES
609

Figure 2.11 Bathymetric map of Clay Lake

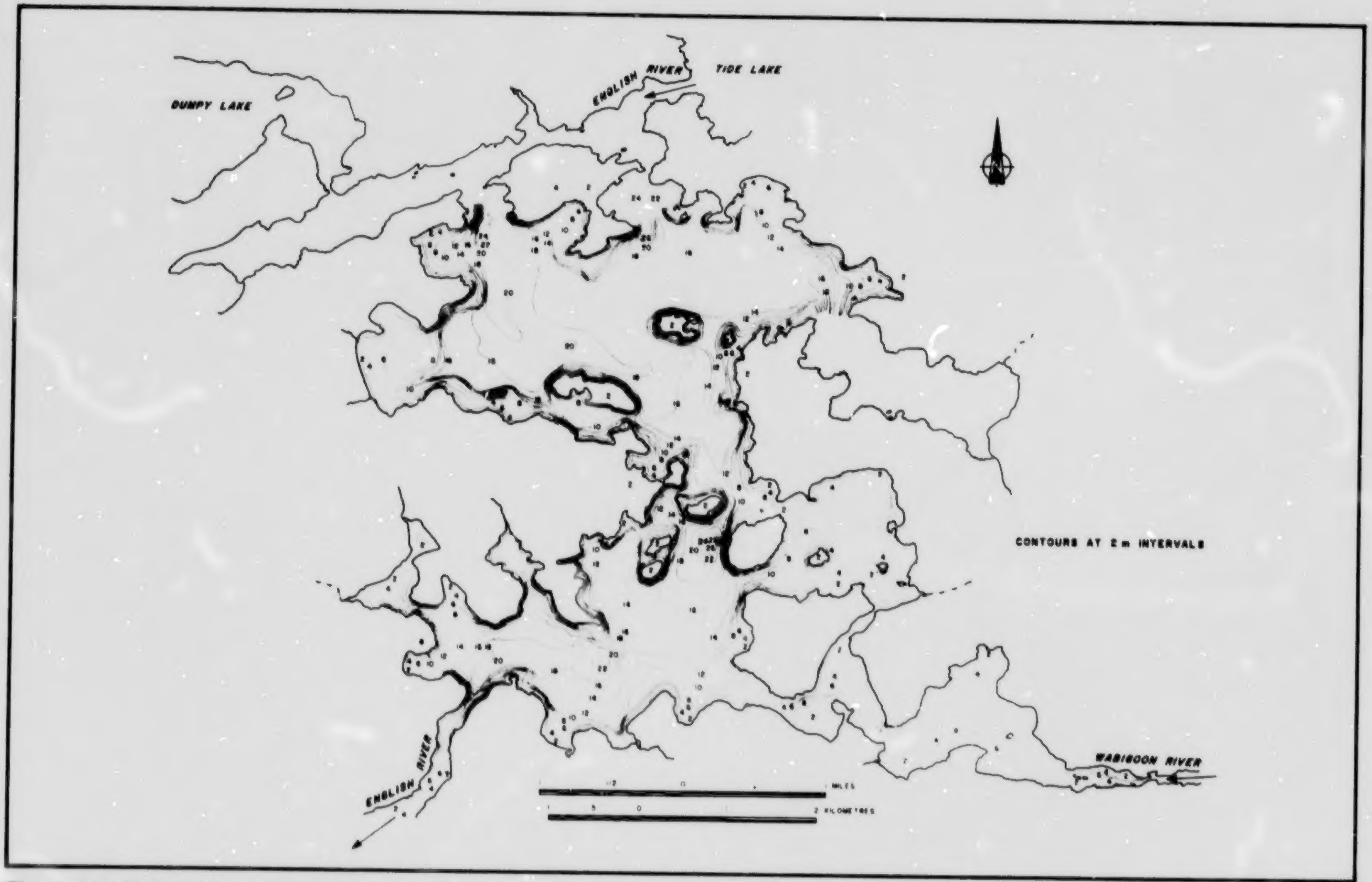
DUMPY LAKE
ENGLISH RIVER
TIDE LAKE
CONTOURS AT 2 m INTERVALS
WABIGOON RIVER
ENGLISH RIVER
1 1/2 0 1 MILES
1 .5 0 1 2 KILOMETRES

Figure 2.12 Bathymetric map of Ball Lake (Courtesy of the Freshwater Institute)

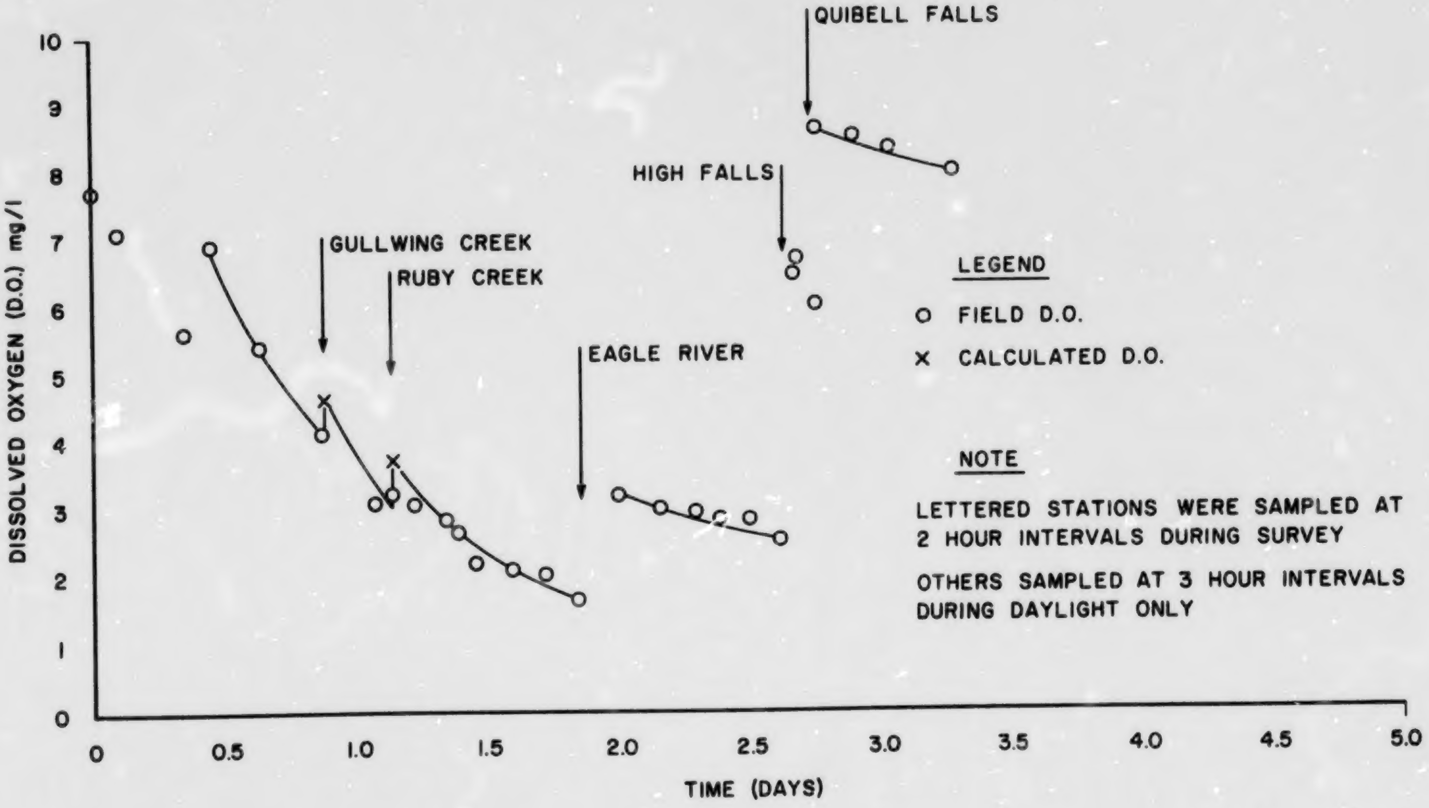

Figure 2.13 Dissolved oxygen (D.O.) profile of the Wabigoon River, 1968.

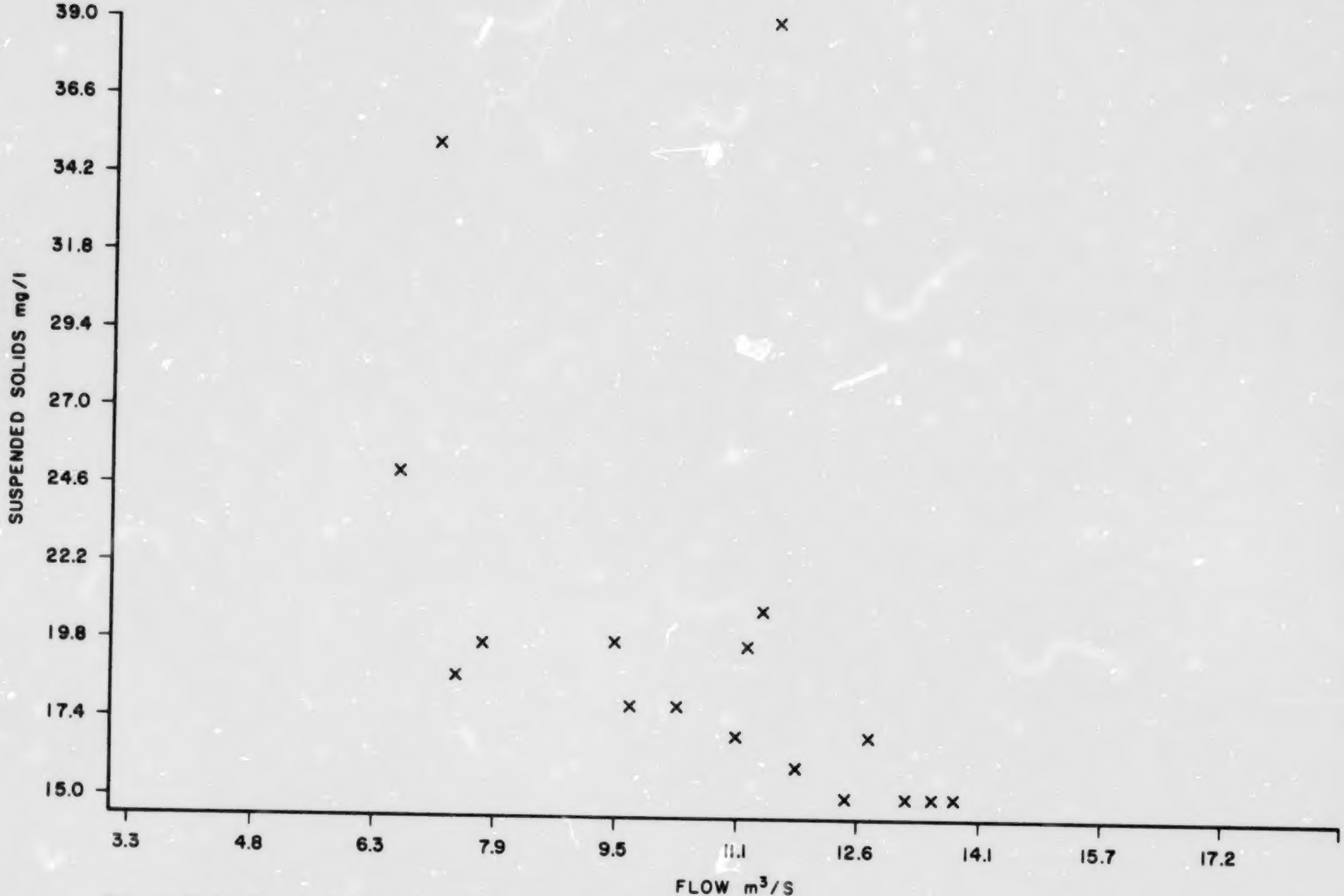

Figure 2.14 Suspended solids-flow relationship for non-high flow periods, Wabigoon River at the inflow to Wainwright Dam.

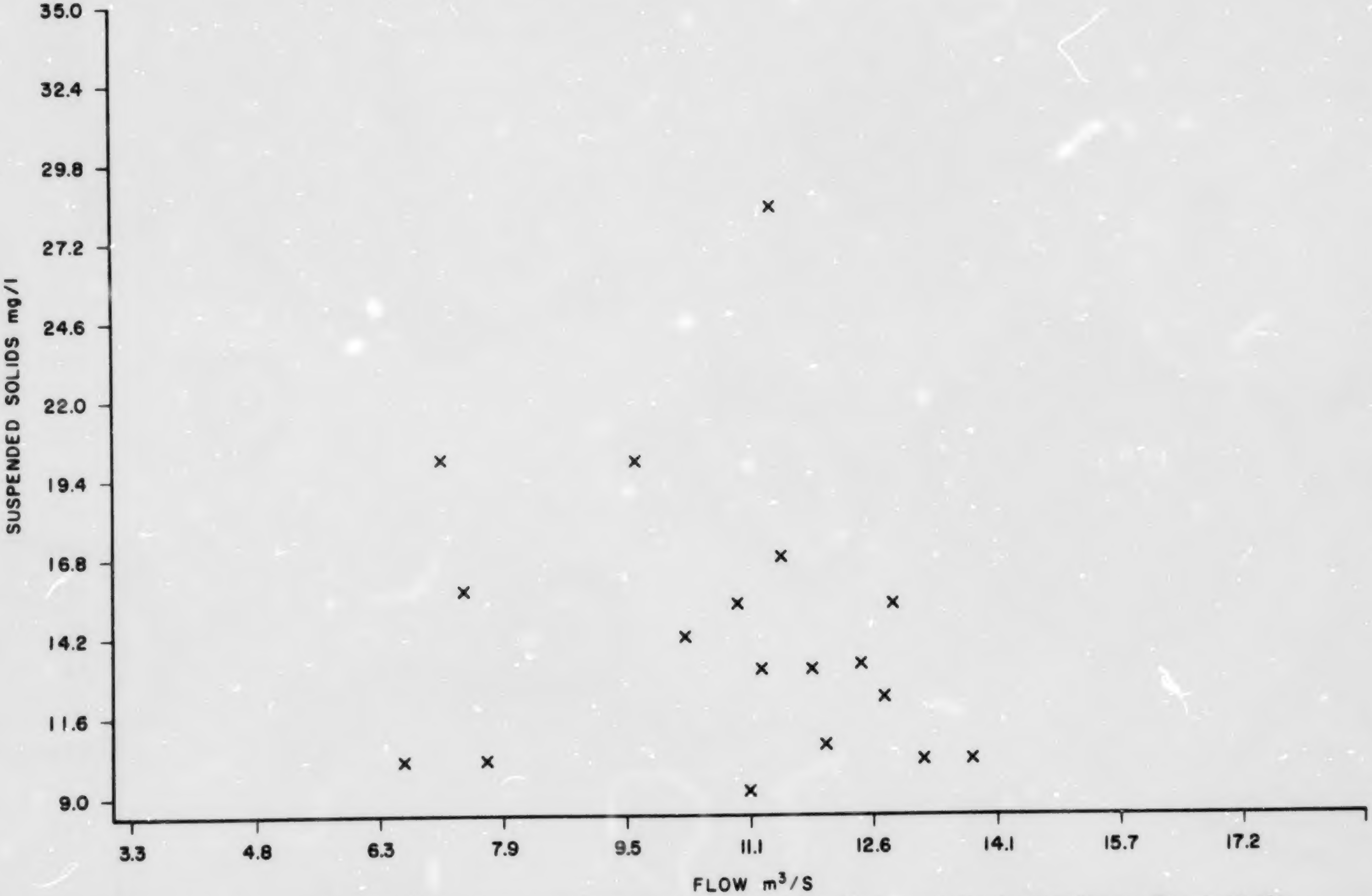

Figure 2.16 Suspended solids-flow relationship for non-high flow periods in Wabigoon River at the outflow of Wainwright Dam.

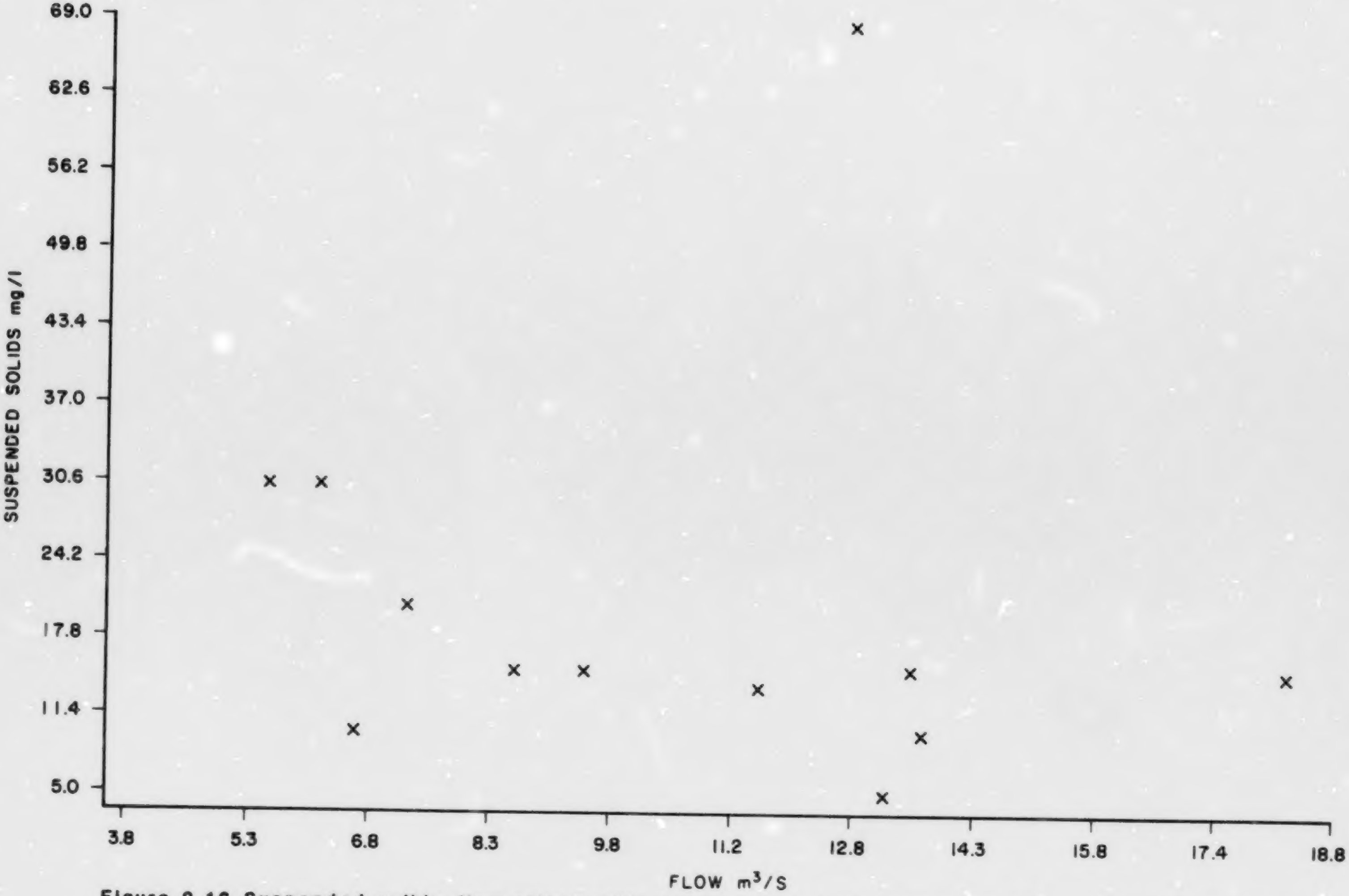

Figure 2.16 Suspended solids-flow relationship for non-high flow periods, Wabigoon River at Minnitaki.

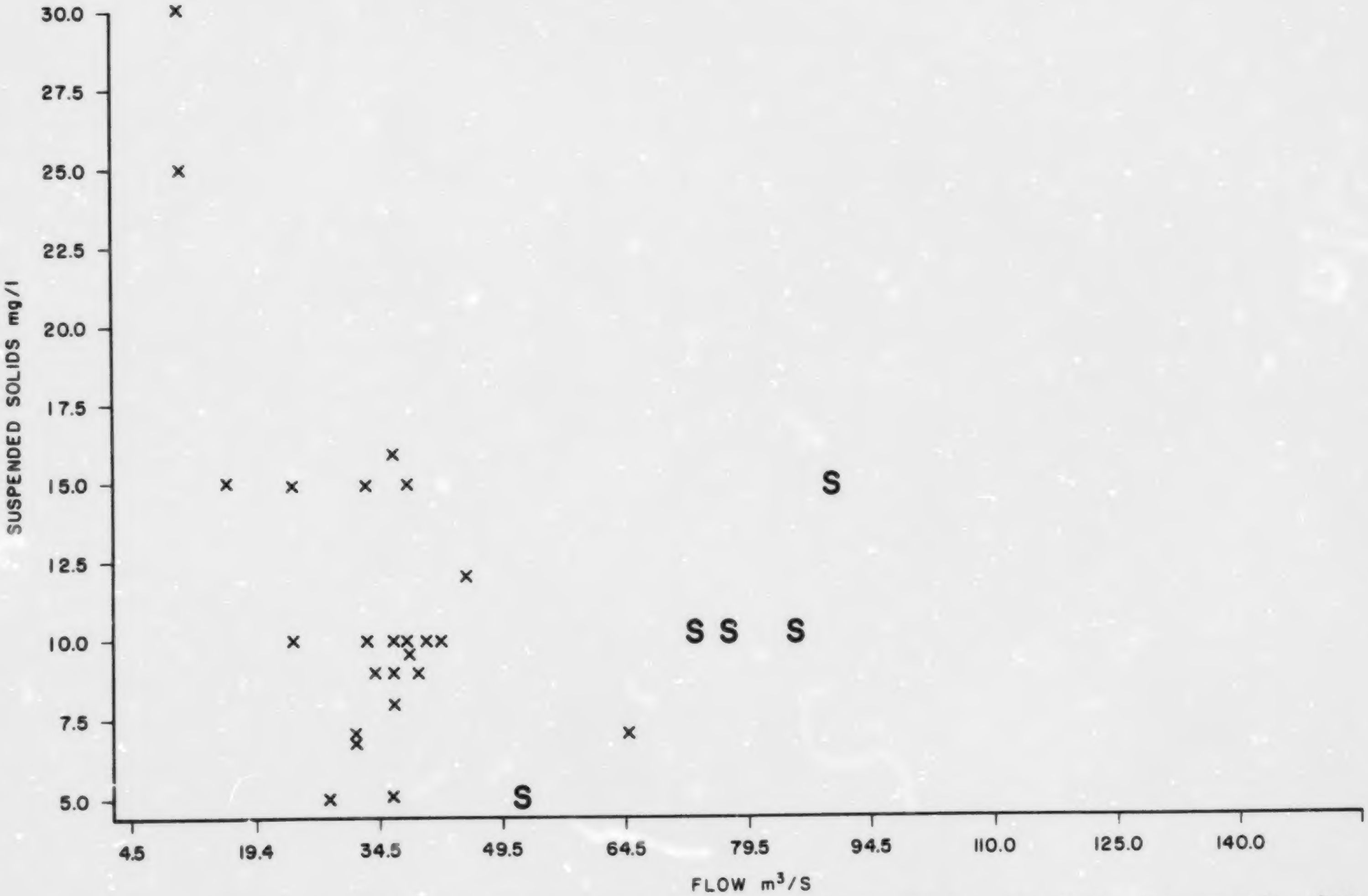

Figure 2.17 Suspended solids -flow relationship, Wabigoon River inflow to Clay Lake. S represents values from 1980 spring runoff.

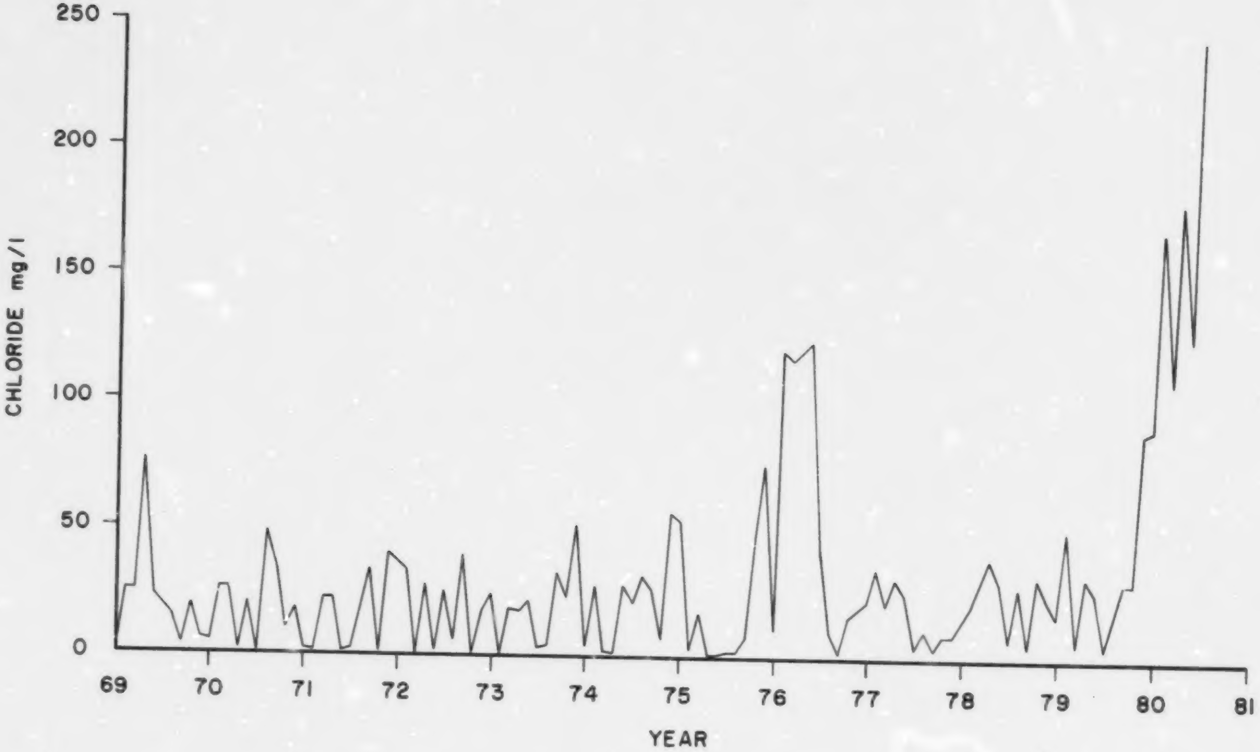

Figure 2.18 Monthly chloride levels in the Wabigoon River downstream of Great Lakes Forest Products Limited, 1969-1980.

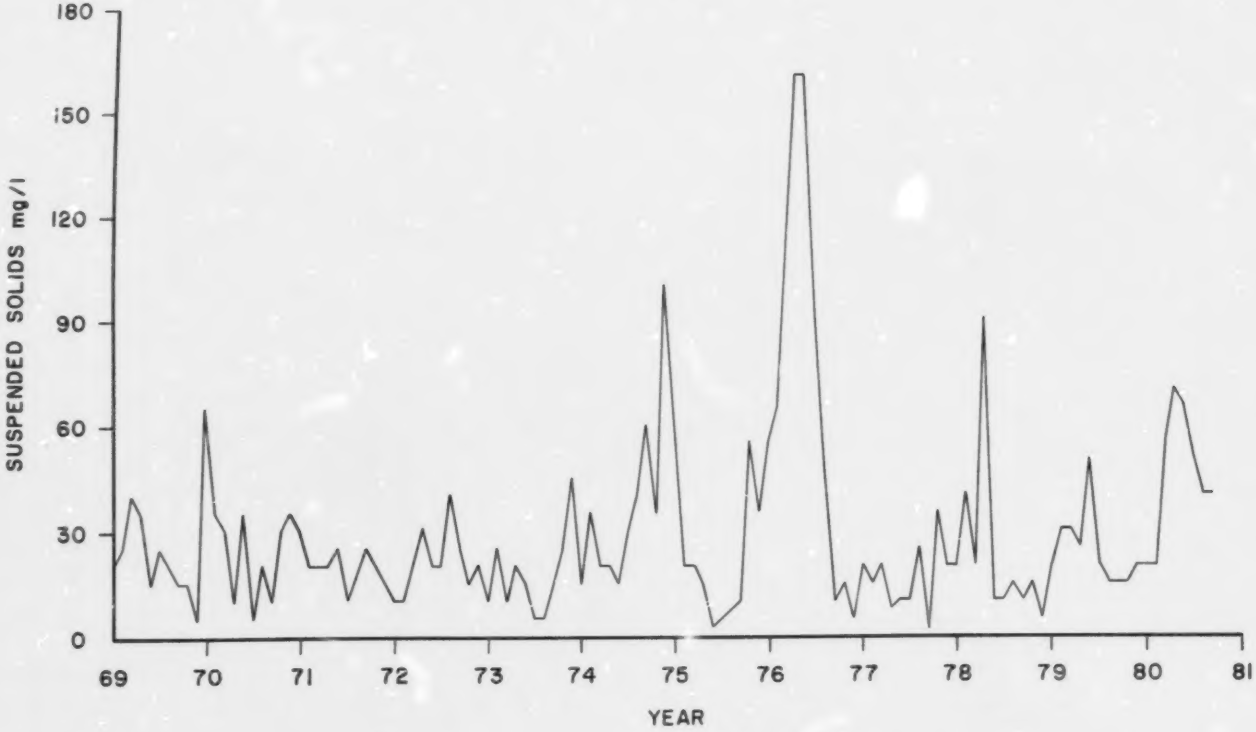

Figure 2.19 Monthly suspended solids for the Wabigoon River downstream of Great Lakes Forest Limited, 1969-1980.

3. MERCURY IN SEDIMENT

3.1 INTRODUCTION

Mercury concentrations in the surface sediments of the Wabigoon/English/Winnipeg River system have been enriched by industrial losses of mercury at Dryden (Armstrong and Hamilton, 1973; Parks, 1976; Jackson, 1979; Jackson and Woychuk, 1980). In Clay Lake sediments, Armstrong and Hamilton (1973) found mercury concentrations ranging from 0.1 µg/g at the mouth of the Wabigoon River to 7.8 µg/g in deeper sections of the eastern basin of Clay Lake. Parks (1976) reported that mercury concentrations in the top 5 cm (centimetres) of sediment decreased with distance downstream from Dryden to the Manitoba border. Decreases from 1970 to 1975 could not be detected, however, due to variability in sampling methods and sample composition. Jackson and Woychuk (1980) recorded highest mercury concentrations (up to 66 µg/g) in wood chip sediments in Wainwright Reservoir. In the eastern and western basins of Clay Lake, mean values were 7.9 and 8.7 µg/g, respectively. Sediments in the south basin of Ball Lake had a mean mercury concentration of 1.2 µg/g.

In the study carried out in the summer of 1980, core samples from lake basins and river sites were collected to determine spatial and temporal trends of total mercury concentrations. In addition, composite grab samples for analysis of total mercury, loss on ignition, and particle size were obtained from the Wabigoon River between Dryden and Clay Lake.

3.2 METHODS

Sediment sampling locations on the Wabigoon/English/Winnipeg River-Lake system, downstream of the Clay Lake inflow, are illustrated in Figure 3.1. Most cores were collected in the centre of major lake basins. For Clay and Ball Lakes, bathymetric data were used to determine basin centres (i.e. maximum depth). For other lakes, lake centres were selected by geographical reconnaissance. As total mercury concentrations have been shown to be relatively homogeneous in lake basin sediments (Armstrong and Hamilton, 1973) duplicate cores were considered adequate for sampling.

Intensive sampling sites on the Wabigoon River between Dryden and Clay Lake are shown in Figure 3.3. For completeness of data, we included results from core sampling conducted in a 300 X 600 m grid (Figure 3.4) at Ball Lake in 1976. In the river survey, cores were acquired from one-quarter, one-half and three-quarters of the horizonal distance across the channel, as the distribution of mercury was assumed to be non-uniform across the channel bed (Parks, 1976). Sediment cores 3.4 cm in diameter and at least 10 cm in length were obtained with a "Phleger-84A" core sampler. The acrylic core tubes, 46 cm in length, were rinsed with acid before use. Care was taken to ensure that the sediment/ water interface remained intact during sampling. The presence of clear water in the upper portion of the tube immediately after sampling suggested that there had been little disturbance of surface sediment. Water above the sediment was carefully removed by suction and a sediment core extractor was used to push the sediment, in 1 cm increments, out of the tube. Each 1-cm increment was sub-sampled with a 2.2 cm diameter glass tube (pre-rinsed with distilled water) and sliced from the core with a stainless steel spatula. This procedure was carried out to prevent cross-contamination from the wall of the tube as the core was pushed in and out. Each 1 cm sample was placed in a labelled, plastic Petri dish and sealed. Sediment characteristics were recorded. Ball Lake cores were divided into sections representing depths of 0-6, 6-8, 8-10, and 10-20 cm.

Figure 3.3 also illustrates locations where grab samples of approximately 5-8 cm of sediment were obtained with a "Ponar" dredge. Samples were collected one-quarter, one-half and three-quarters of the horizontal distance across the river channel, then combined to form a composite sample. Sediments were placed into acid-rinsed, 0.4-litre glass jars with ceramic lids, and substrate characteristics recorded.

Cores and grab samples were analyzed by acid digestion followed by flameless atomic absorption (Loescher and Neary, 1981), at the Ontario Ministry of the Environment laboratory in Toronto. Analyses for loss on ignition and particle-size (sand, silt and clay) were also carried out on grab samples by the same laboratory.

3.3 RESULTS AND DISCUSSIONS

(a) Major Lake Basins

Total mercury concentrations in each of the first 10 cm of sediments from major lake basins of the Wabigoon/English/Winnipeg River/Lake system are reported in Table 3.1. Ball Lake data for 1976 are shown in Table 3.2. With the exception of Eaglenest Lake, these data are illustrated as profiles in Figures 3.1 and 3.2. Large amounts of sand were present in Eaglenest sediment, in contrast to the clay and silt at other sites. Because the adsorption capacity for mercury varies with sediment type (Townsend, et al., 1974; Reimers, et al., 1974), comparisons of mercury concentrations should be made between samples from similar sediments. All sediments except those from Eaglenest Lake comprised clay and silt covered with a thin layer of loose, brownish floc. Particle-size analysis is shown in Table 3.3 for Ball Lake sediment. Similar data for Clay Lake may be found in Armstrong and Hamilton, (1973).

The sediment profiles show that mercury contamination is confined to the top few centimetres. Mercury levels decrease with increasing distance downstream of Dryden. Sites can be grouped into three categories. In the first group are both basins of Clay Lake, where total mercury concentrations exceed 1 µg/g in surface sediment. In the second group are all sites on the English River system and Sand Lake, where mercury in surface sediments is about 0.5 µg/g. The third group includes control sites (Wabigoon

Lake, Maynard Lake) with mercury levels below 0.1 μg/g. The data show that mercury levels were less than 0.1 μg/g below a depth of about 5 cm in sediment at all major basin sites.

Enrichment factors (ratio of surface concentration to concentration at depth) in the sediment profiles are as high as 30 in the eastern and western basins of Clay Lake, then decline to 9 in the south basin of Ball Lake, 7 in Lount Lake, and 5 in Umfreville Lake. An enrichment factor of 5 was found in Sand Lake, probably as a result of mercury-based slimicides discharged to the Winnipeg River by Boise Cascade Canada Limited, Kenora, between 1960 and 1967 (Neary, 1976).

Variations in mercury concentrations of sediments from the eastern and western basins of Clay Lake are illustrated in Figures 3.5 and 3.6, respectively, where data from our study are compared with results from earlier surveys. In cores for 1971, mercury was highest at the sediment/water interface, due to the large industrial mercury loadings at Dryden. Cores obtained in 1978 and 1980, after industrial loadings ceased, had much less mercury in surface sediment, presumably because of natural restorative processes. Differences in mercury concentrations between our cores and those obtained by Rudd et al.(1980) are probably due to differences in sampling methods and location.

The eastern basin of Clay Lake does not stratify in summer. Sediments here are subject to resuspension and strong wave action. Mercury-enriched suspended particulate matter carried by the Wabigoon River settles in the eastern basin, a process which may be particularly important during spring runoff. Differences in sedimentation rates within the eastern basin might account for the differences in mercury levels between the 1978 and 1980 profiles. In 1980, mercury concentrations in the surface sediment (0-1 cm depth) were lower than those in deeper horizons.

Core profiles for the western basin of Clay Lake (Figure 3.6) also illustrate burial of contaminated sediments. In 1980, mercury concentrations at the 0-1 cm depth were 2.2 and 3.3 μg/g, compared to 6.9 and 6.5 μg/g at a depth of 2-3 cm in the same cores.

Mercury in surface sediment in Ball Lake was about one order of magnitude lower than that in comparable sediment in Clay Lake. In the top 6 cm of sediment in the south basin of Ball Lake, the mercury concentration was 0.12 μg/g. This value is lower than the mean of 0.25 μg/g for 26 cores sampled here in 1976. The mercury profile, however, does not suggest any temporal decrease since the mercury concentration in the surface (0-1 cm) layer is the highest in the core. The 1976 survey (Figure 3.4, Table 3.2) revealed no mercury enrichment of surface sediment in the north basin. Lake morphology and currents may have prevented the movement of anthropogenic mercury into this part of Ball Lake. Highest mercury concentrations in the south basin were restricted to two areas: near the mouth of the main channel of the Wabigoon River, and at the western end of the lake near the English River outflow. The narrow range of values in the southern basin is attributed to substrate homogeneity.

At Lount and Umfreville Lakes, the occurrence of lower mercury levels in surface sediment (0-1 cm depth) than at slightly greater depth suggests that conditions may be improving in this portion of the system.

The Sand Lake profile indicates that surface sediment is the most contaminated layer despite the cessation, in 1967, in use of mercury-containing slimicides at a pulp and paper mill upstream at Kenora. The surface layer (0-1 cm) of sediment in this lake contained about the same amount of mercury as sediment in the south basin of Ball Lake, Lount Lake and Umfreville Lake.

(b) Wabigoon River

Sediment in the Wabigoon River is composed of sand and gravel, silt, clay, iron sulphide, bark, chips, wood fibres, leaves, snail shells, and other organic debris. Wood fragments were dominant in most samples. Particle size analysis is given in Table 3.5. Organic material was found in distinct layers or intermixed with other substrate. The abundance of organic matter is important, because Townsend et al. (1974) have shown wood fibre and fine particles to have a higher sorption capacity for mercury than sand. Kudo and Hart (1974) also concluded that fine particles and wood chips had a significant portion of the mercury existing within bed sediments. Remobilization of mercury in these sediments can arise from physical resuspension during spring runoff or from desorption. Mercury analyses of sediment cores from sites below the Wainwright Dam are presented in Table 3.4 and Figures 3.2 and 3.7.

Sediments in the Wainwright Dam reservoir comprise wood chips and bark. These sediments are estimated to be from 3 to 12 m thick (Parks, 1976; Jackson, 1980) and were not amenable to coring. Our sampling of the reservoir and the river upstream was limited to three composite samples in the top 5 cm of sediments. Mercury concentrations in this layer ranged from 1.4-1.8 µg/g, levels which were much lower than those found by Jackson (1980). In cores from the woodchip and bark layer, he found mercury ranging from 6.8 to 43 µg/g upstream of the reservoir, and from 5.2 to 66 µg/g in the reservoir itself. Jackson estimated that the total sedimentary mercury burden in the Wabigoon River between Dryden and the Wainwright Dam was 990-3650 kg (kilograms).

Immediately downstream of the Wainwright Dam, large beds of wood chips and bark are deposited on the river banks. Cores just below the Wainwright Dam had the highest mercury concentrations of any samples collected, with levels above 10 µg/g at depths of 10 cm. Lower mercury concentrations were usually found in cores from the centre of the stream, where scour processes would have removed fine particles of mercury-rich organic materials.

As distance downstream of Dryden increased, the quantity of organic material decreased (Figure 3.8). Intermediate increases in this declining trend occurred just upstream natural rock barriers, where fine particulate matter, including organic material, has probably settled. Mercury concentrations peaked at the same locations (Figure 3.9) as organic matter (Figure 3.8). A curve of mercury concentrations regressed on values for loss on ignition yielded a correlation coefficient of 0.86 (Figure 3.10).

In the river, the highest mercury levels were generally found in deeper sections of the cores. This phenomenon suggests that either substantial quantities of mercury have been desorbed or that sediments with highest mercury concentrations have been covered with less contaminated material. Record high flows in 1974 may possibly also have redistributed sediments.

Based on sediment core data, we estimated that 1300 kg of anthropogenic mercury was contained in sediments in the Wabigoon River between the Wainwright Dam and Clay Lake inlet (Table 3.6). Figure 3.11 illustrates the quantities of mercury occurring in eight segments of the river. Our data suggest that Jackson's 1980 estimate of 740 kg may be low. Armstrong and Hamilton (1973) estimated that 2000 kg of total mercury were present in the top 6 cm of sediments in Clay Lake. Assuming minimal removal of sedimentary mercury from the lake since 1971, the total estimated mercury from Dryden to the outlet of Clay Lake would be 4,300-7,000 kg, or 47-77 percent of the original amount of mercury discharged at Dryden.

Sediment samples were also collected in midstream at two sites in the Wabigoon River between Clay and Ball Lakes. The first site, WS, was about equidistant from Clay and Ball Lakes (near Segise Lake), while the second station, WRI, was located just upstream of Ball Lake (Table 3.4). Both sites were selected in quiet reaches of the river. Samples were mainly clay and silt, although there were large amounts of fine sand, particularly upstream of Ball Lake. Samples from this area show that surface sediment is enriched with mercury (Table 3.4) and that, unlike river sites upstream of Clay Lake, mercury concentrations were highest in the surface layer of sediment.

Figure 3.12 shows particle size distribution for grab samples. Particles larger than 4.75 mm, mainly wood chips and bark in the upper reaches of the river, were removed from samples before analysis. Because the trend for sand and gravel was very similar to that for loss on ignition (Figure 3.9) for a distance of about 55 km downstream of Dryden, much of the "sand and gravel" in Figure 3.12 may have really been samll wood particles. This interpretation is enforced by field observations, which showed little sand and gravel in this part of the river. Visual field observations from 65 km downstream confirmed the presence of sand and gravel in sediment, hence the sharp rise in sand shown in Figure 3.12 at this point.

3.4 CONCLUSIONS

1. Mercury concentrations in surface sediments in the Wabigoon/ English/ Winnipeg River system were elevated in comparison to background values of 0.01-0.10 μg/g.

Highest mercury concentrations occurred in sediments near Dryden, where levels of 10-15 µg/g were common. Mercury in the eastern and western basin sediments of Clay Lake, the first lake downstream of Dryden, ranged from 3-6 µg/g. Concentrations in lakes in the English River system were approximately one order of magnitude below values for Clay Lake sediment, but were still above normal. Surface sediment in Sand Lake, on the Winnipeg River system upstream of the English River confluence, had mercury levels similar to those of the contaminated English River system. Elevated mercury in Sand Lake may be the result of industrial losses at Kenora.

2. Mercury in Wabigoon River sediment was much more variable than that from lake basins.
3. Mercury concentrations at the sediment surface were usually lower than values at slightly greater depth. This finding suggests that improvement has occurred through the accumulation of 10 years of "clean" sediment. This situation did not apply to Ball Lake, where highest mercury concentrations were found at the sediment surface. In Ball Lake, the Wabigoon River may still be depositing significant amounts of mercury or, alternatively, sedimentation rates may be very low.
4. Large quantities of mercury remain in the Wabigoon River upstream of Clay Lake. Much of this mercury is associated with organic matter which has accumulated behind artificial and natural dams.

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TABLE 3.1. Total mercury concentrations (µg/g, dry weight) in sediment cores from major lake basins of the Wabigoon/English/Winnipeg River system.

Site	Depth (cm) 0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	9-10
Wabigoon Lake	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Clay Lake, Eastern Basin	2.8 3.1	3.9 3.7	8.1 5.1	2.8 0.33	0.36 0.25	0.13 0.09	0.11 0.09	0.12 0.04	0.12 0.07	0.03 0.04
Clay Lake, Western Basin	3.3 2.2	5.1 4.6	6.5 6.9	0.05 0.34	0.07 0.10	0.08 0.07	0.07 0.08	0.06 0.07	0.02 0.07	0.03 0.08
Maynard Lake	0.08	0.06	0.05	0.07	0.07	0.06	0.07	0.06	0.05	0.05
Ball Lake, Southern Basin	0.36	0.16	0.11	0.04	0.03	0.05	<0.01	0.17	0.03	0.04
Lount Lake	0.42 0.48	0.47 0.33	0.35 0.27	0.18 0.18	0.07 0.12	0.10 0.10	0.09 0.09	0.07 0.10	0.07 0.08	0.05 0.08
Umfreville Lake, Western Basin	0.28 0.24	0.54 0.35	0.10 0.11	0.07 0.11	0.06 0.11	0.05 0.09	0.07 0.08	0.06 0.08	0.03 0.07	0.05 0.07
Sand Lake	0.53 0.40	0.35 0.25	0.13 0.23	0.08 0.09	0.09 0.07	0.04 0.05	0.04 0.05	0.04 0.07	<0.01 0.05	<0.01 0.08
Eaglenest Lake	0.04 (5 cm composite)									

TABLE 3.2. Mercury profiles (μg/g dry weight) for selected cores, Ball Lake, July, 1976.

Site[a]	Mercury concentration at indicated depths			
	0-6 cm	6-8 cm	8-10 cm	10-20 cm
South Basin, centre	0.33	0.09	0.07	0.06
South Basin, southeast corner	0.17	0.07	0.09	0.06
North Basin, centre	0.07	0.07	0.08	
North Basin, northwestern bay	0.03	0.03	0.03	0.03

[a] See Figure 3.3.

TABLE 3.3. Particle size analysis on selected sediments, Ball Lake, July, 1976.

Site[a]	% sand	% silt	% clay
South Basin, southwest corner	2	14	83
South Basin, centre	<1	22	77
North Basin, southeast corner	<1	16	82
North Basin, north corner	<1	19	79

[a] See Figure 3.3.

TABLE 3.4. Total mercury concentrations (µg/g, dry weight) in sediment cores from Wabigoon River, Dryden to Ball Lake, 1980.

Sediment Sampling Site	Subsample[b] Location	Depth (cm)										
		0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	9-10	15-20
12 km downstream of Dryden (5A)	R	29.0	31.0	21.0	26.0	26.0	27.0	26.0	9.40	9.00	15.00	0.06
	C	0.79	0.73	0.04	0.02	0.02	0.02	0.02	0.02	0.01	<0.01	
	L	27.0	25.0	18.0	16.0	8.9	6.50	9.60	13.00	13.00	24.00	5.10
18 km downstream of Dryden (5B)	R	7.30	2.20	1.40	0.98	0.21	0.08	0.03	0.03	0.03	0.02	
	C	4.50	6.70	6.90	10.00	15.00	14.00	18.00	14.00	2.9	0.05	0.02
	L	5.60	6.30	11.0	12.00	13.00	12.00	9.20	10.00	11.00	2.30	0.05
25 km downstream of Dryden (5C)	R	2.10		1.50		4.80		6.1	6.7	12.00	6.50	
	C	1.40	1.60	0.15	0.06	0.04	0.05	0.04	0.02	0.02	0.02	0.02
	L	0.70	2.00	3.00	2.80	10.00	2.80	0.65	0.16	<0.01	<0.01	
Minnitaki Road (6)	R	2.60	3.80	4.50	6.50	7.20	4.10	2.4	0.29	0.02	0.03	
	C	3.20	4.30	3.80	3.70	0.53		0.01	<0.01	0.01	<0.01	
	L	2.90	3.40	4.00	4.50	4.00	7.30	15.00	17.00	4.00	0.11	
0.5 km upstream of Eagle River confluence (6A)	R	3.10	2.60	0.21	<0.01	0.02	0.01	<0.01	<0.01	0.01	0.01	
	C	1.10	0.09	0.04	0.03	0.03	0.02	0.01	0.03	<0.01	<0.01	
	L	2.50	2.90	3.70	1.90	0.08	0.04	0.04	0.02	0.02	0.03	0.02
Eagle River (2)	C	0.05	0.07	0.05	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
9.8 km downstream of Eagle River confluence (6C)	R	10.00	15.00	15.00	14.00	20.00	23.00	8.6	3.2	0.06	0.03	0.03
	C	2.1	0.48	0.03	<0.01	<0.01	0.01	0.01	<0.01	0.02	0.01	<0.01
	L	3.8	3.5	0.76	0.09	<0.01	<0.01	0.01	0.01	0.01	0.02	<0.01
Red Lake Highway (6D)	R	0.97	0.67	0.58	0.56	0.44	0.02	<0.01	<0.01	<0.01	<0.01	
	C	0.16	0.04	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
	L	0.28	0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	
Approx. mid-way between Clay and Ball Lakes (WS)	C	1.60	1.50	0.19	0.06	0.02	0.04	0.05	0.05	0.01	0.06	
Upstream of Ball Lake (WR1)	C	1.29	1.13	.94	.72	.52	.06	.02	<.01	.02	<.01	

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[a] See Figure 3.1.

[b] At quarter points across the channel, facing upstream - R=right, C=centre, L=left.

TABLE 3.5. Total mercury concentrations (μg/g, dry weight), particle-size, and organic matter (% dry weight) in grab samples of sediments from the Wabigoon River from Dryden to Clay Lake.

Distance Downstream from Dryden (km)	Organic Matter (loss on ignition)	Total Mercury (μg/g, dry weight)	Particle-Size (%)		
			Gravel & Sand	Silt	Clay
12	61	12	70	19	12
14	23	5.0	36	29	35
17	41	7.6	43	28	29
19	33	12	36	33	31
22	14	3.9	11	42	47
25	9	3.1	9	53	38
27	23	10	20	38	42
30	18	18	10	45	45
33	18	9.2	9	48	43
36	10	4.4	9	43	48
38	16	6.5	6	46	48
52	18	8.4	4	52	44
44	17	13			
44	20	9.1	4	54	42
46	22	5.8	8	45	47
47	22	9.0	4	56	40
50	10	1.5	2	56	42
52	11	1.9	6	50	44
53	16	6.7	3	43	54
56	12	4.0	2	50	47
58	19	5.8	3	43	55
61	19	3.4	1	45	55
66	7	0.59	12	66	22
70	5	1.0	55	35	10
73	7	0.79	18	65	17
76	6	0.66	26	61	14
79	4	0.62	61	30	9
82	5	0.65	46	41	13

TABLE 3.6. Estimated quantities (kg) of anthropogenic mercury in the Wabigoon River and Clay Lake.

Location	Quantity of Mercury	Cumulative Total	% of Total Mercury Discharged (9080 kg)
Wabigoon River, from Dryden to, and including, Wainwright reservoir[a]	1000-3600	1000-3100	11-40
Wabigoon River, Wainwright dam to 30 km downstream of Dryden	980	2000-4600	22-51
Wabigoon River, 30 km downstream of Dryden to Inlet of Clay Lake	330	2300-4900	25-55
Clay Lake[b]	2000	4300-6900	47-77

[a] Jackson (1980).

[b] Armstrong and Hamilton (1973).

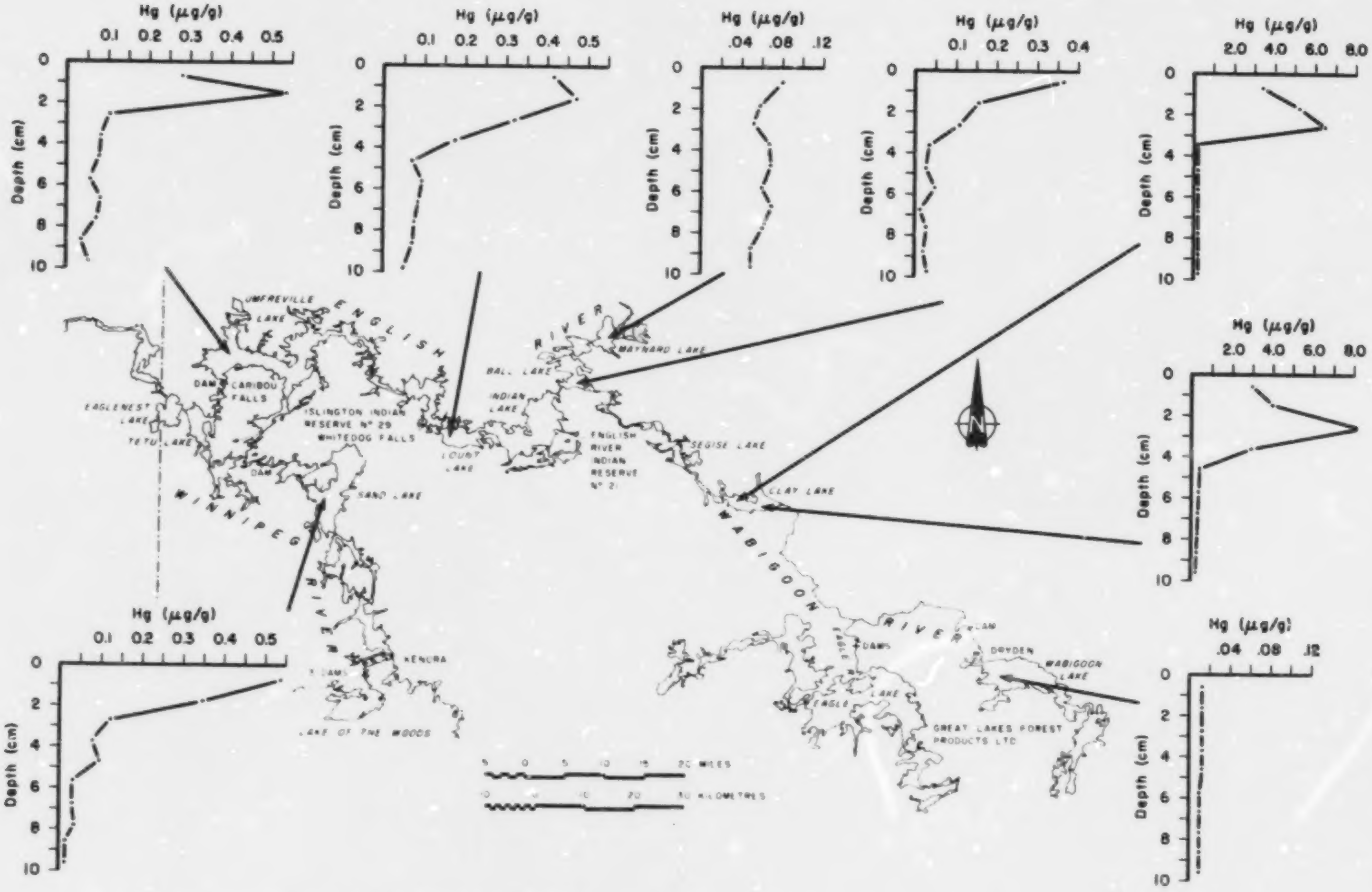
Hg (μg/g)
Depth (cm)
0.1 0.2 0.3 0.4 0.5
.04 .08 .12
2.0 4.0 6.0 8.0
0 2 4 6 8 10
UMFREVILLE LAKE
ENGLISH RIVER
MAYNARD LAKE
BALL LAKE
INDIAN LAKE
CARIBOU FALLS
DAM
EAGLENEST LAKE
TETU LAKE
ISLINGTON INDIAN RESERVE Nº 29
WHITEDOG FALLS
LOUNT LAKE
ENGLISH RIVER INDIAN RESERVE Nº 21
SEGISE LAKE
CLAY LAKE
WINNIPEG RIVER
SAND LAKE
KENORA
2 DAMS
LAKE OF THE WOODS
WABIGOON RIVER
EAGLE LAKE
DAMS
DAM
DRYDEN
WABIGOON LAKE
GREAT LAKES FOREST PRODUCTS LTD
5 0 5 10 15 20 MILES
10 0 10 20 30 KILOMETRES

Figure 3.1 Mercury in sediment profiles from lakes in the Wabigoon/English/Winnipeg River system, 1980.

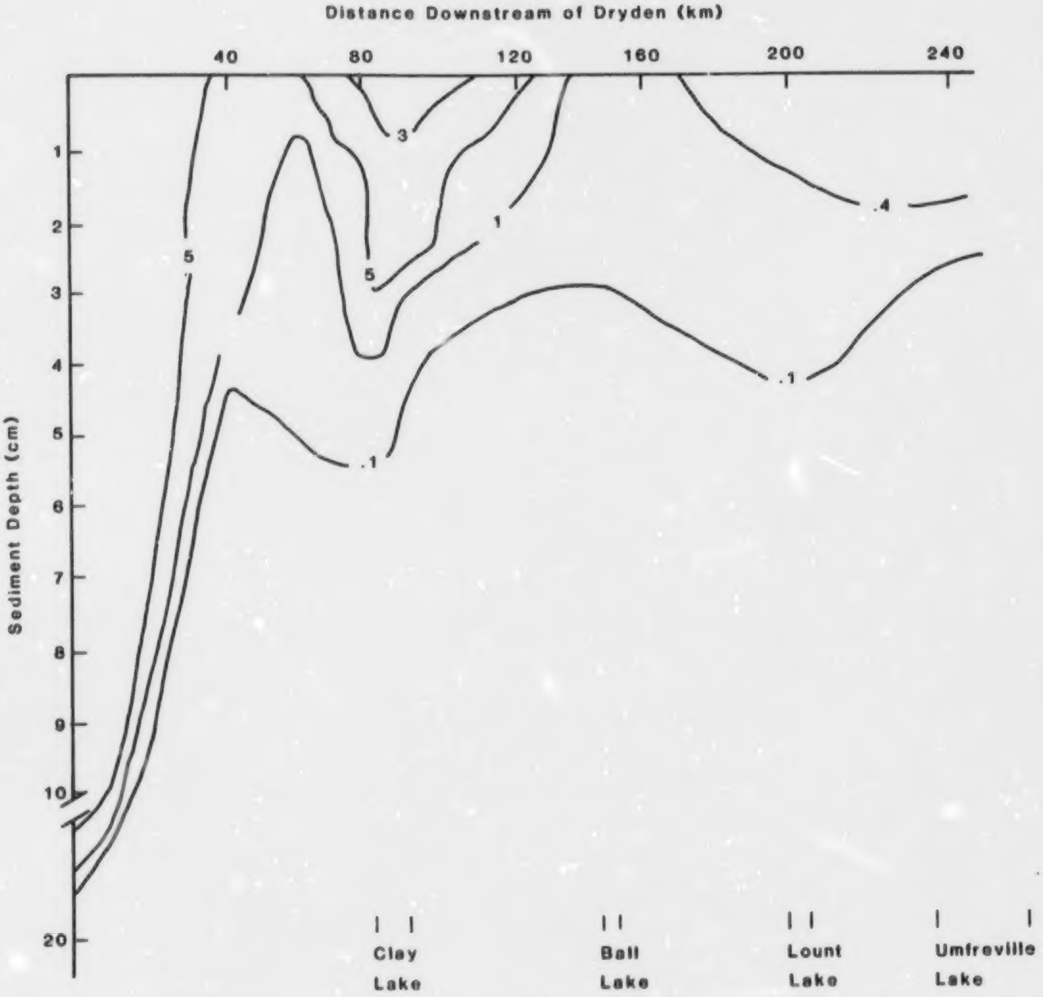

Figure 3.2 Mercury concentration contours (ug/g), (dry weight), for surface sediments , Wabigoon/English River System, 1980.

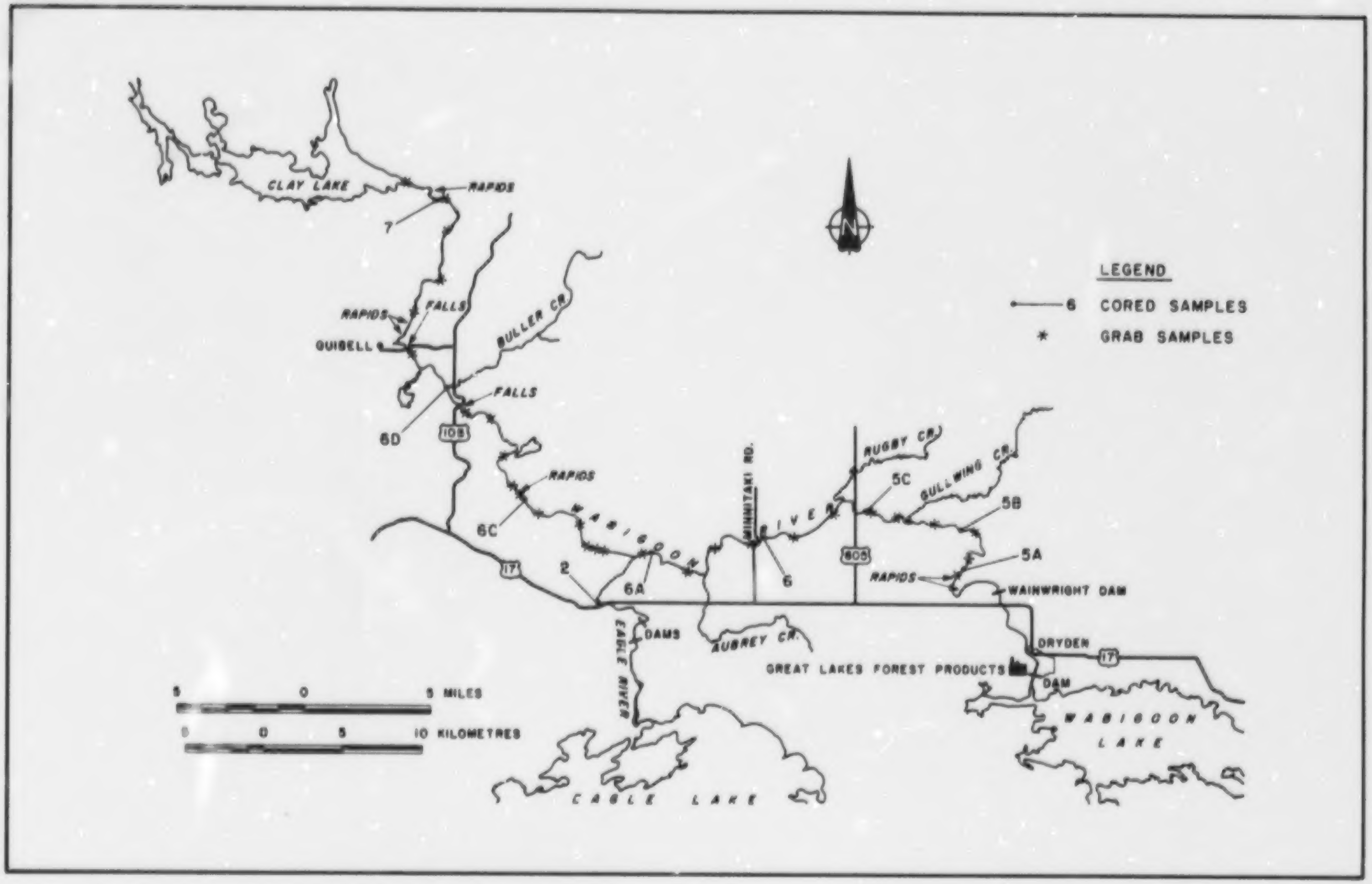
CLAY LAKE
RAPIDS
7
RAPIDS
FALLS
QUIBELL
BULLER CR.
FALLS
6D
108
RAPIDS
6C
WABIGOON
2
6A
17
MINNITAKI RD.
RIVER
6
805
RUGBY CR.
5C
GULLWING CR.
5B
5A
RAPIDS
WAINWRIGHT DAM
DRYDEN
17
GREAT LAKES FOREST PRODUCTS
DAM
WABIGOON LAKE
DAMS
EAGLE RIVER
AUBREY CR.
EAGLE LAKE
N
LEGEND
6 CORED SAMPLES
* GRAB SAMPLES
5 0 5 MILES
5 0 5 10 KILOMETRES

Figure 3.3 Wabigoon River sediments sampling site, 1980

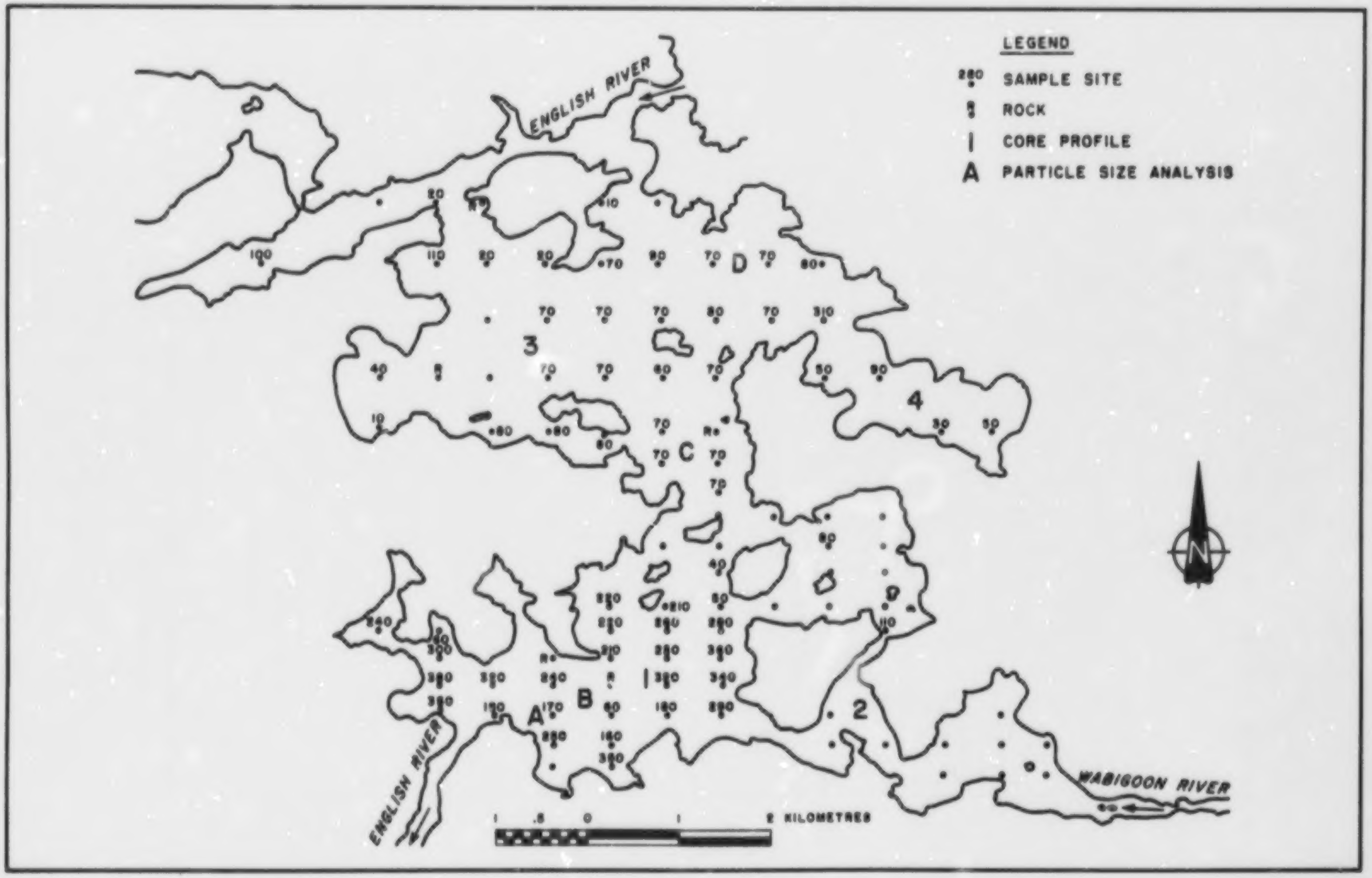
LEGEND
SAMPLE SITE
ROCK
CORE PROFILE
A PARTICLE SIZE ANALYSIS
ENGLISH RIVER
ENGLISH RIVER
WABIGOON RIVER
N
1 .5 0 1 2 KILOMETRES
A
B
C
D
2
3
4

Figure 3.4 Mercury (ng/g, dry weight) in upper 6 cm of sediment, Ball Lake, 1976.

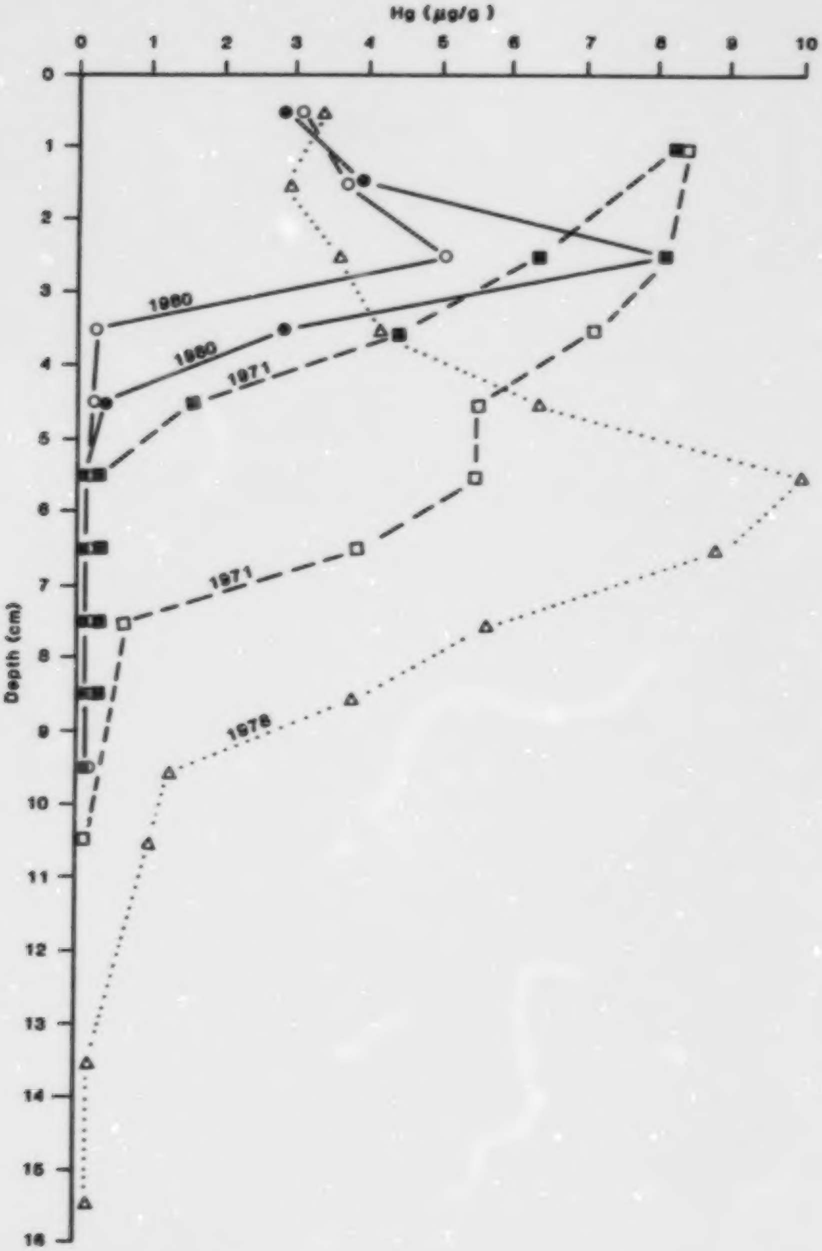

Figure 3.5 Variation in Mercury concentration with depth Clay Lake eastern basin 1971 1975 and 1980

a-From Armstrong and Hamilton (1973)
b-From Rudd ET AL (1980)

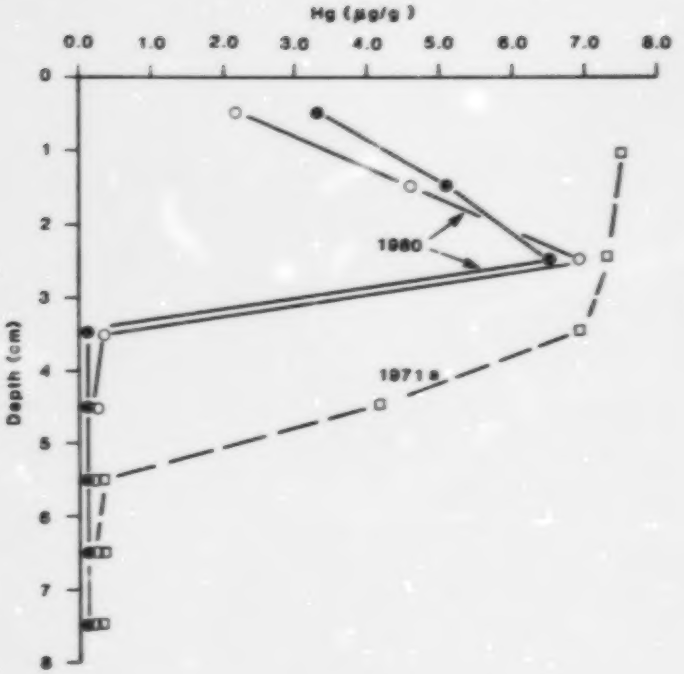

Figure 3.6 Variation in Mercury concentration with depth
Clay Lake western basin 1971 and 1980

a-From Armstrong and Hamilton (1973)

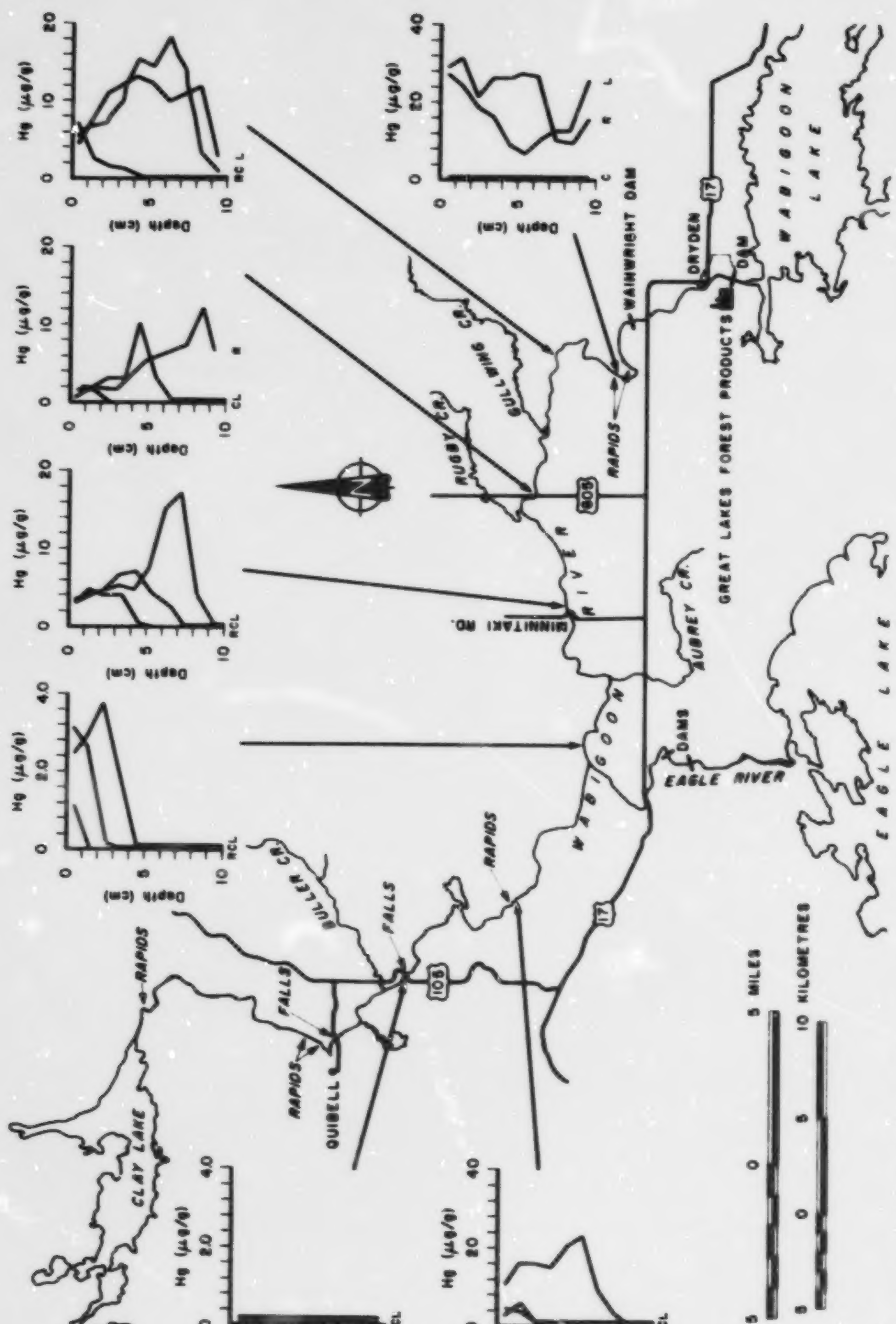
Hg (µg/g)
Depth (cm)
0
5
10
20
40
2.0
4.0
RCL
R
C
L
CL
CLAY LAKE
RAPIDS
FALLS
QUIBELL
BULLER CR.
105
RAPIDS
WABIGOON
RIVER
17
EAGLE RIVER
DAMS
EAGLE LAKE
AUBREY CR.
MINNITAKI RD.
605
RUGBY CR.
GULLWING CR.
RAPIDS
WAINWRIGHT DAM
DRYDEN
DAM
GREAT LAKES FOREST PRODUCTS
WABIGOON LAKE
N
5 MILES
10 KILOMETRES

Figure 3.7 Mercury in Wabigoon River sediment profiles

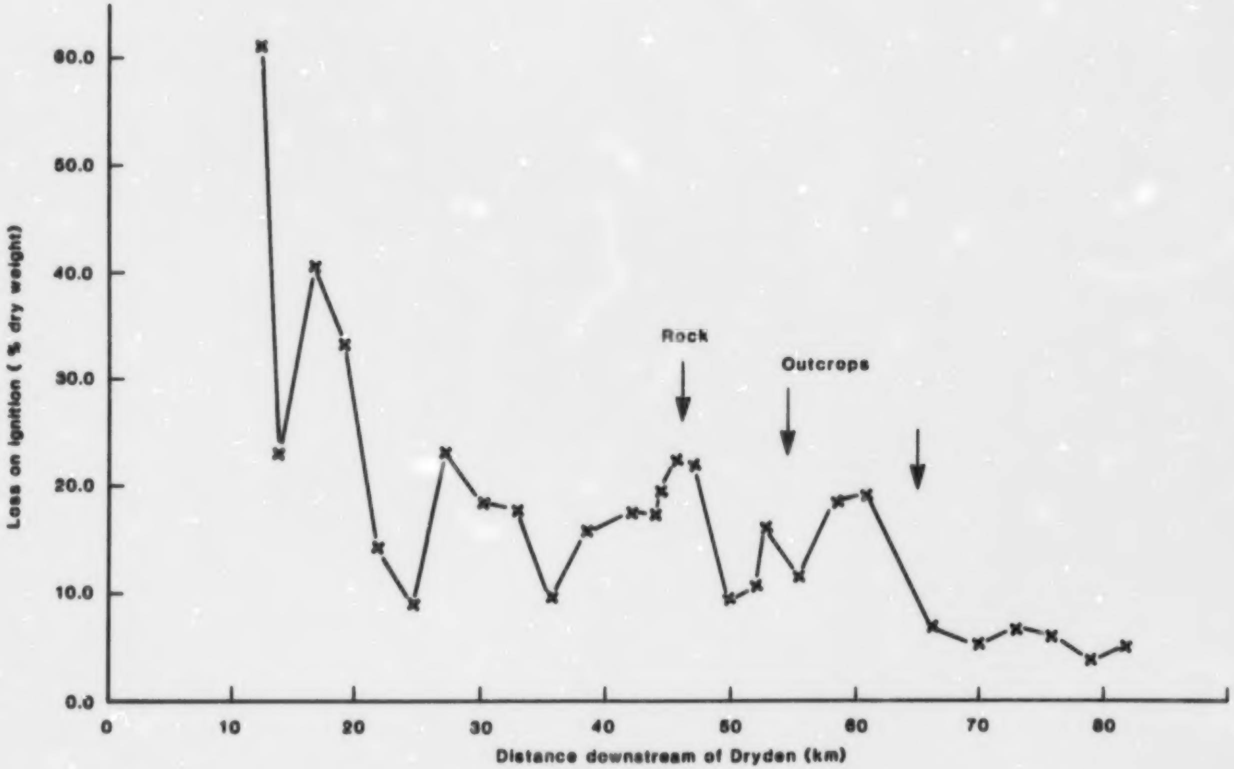

Figure 3.8 Organic matter (loss on ignition) in sediments in the Wabigoon River from Dryden to Clay Lake 1980.

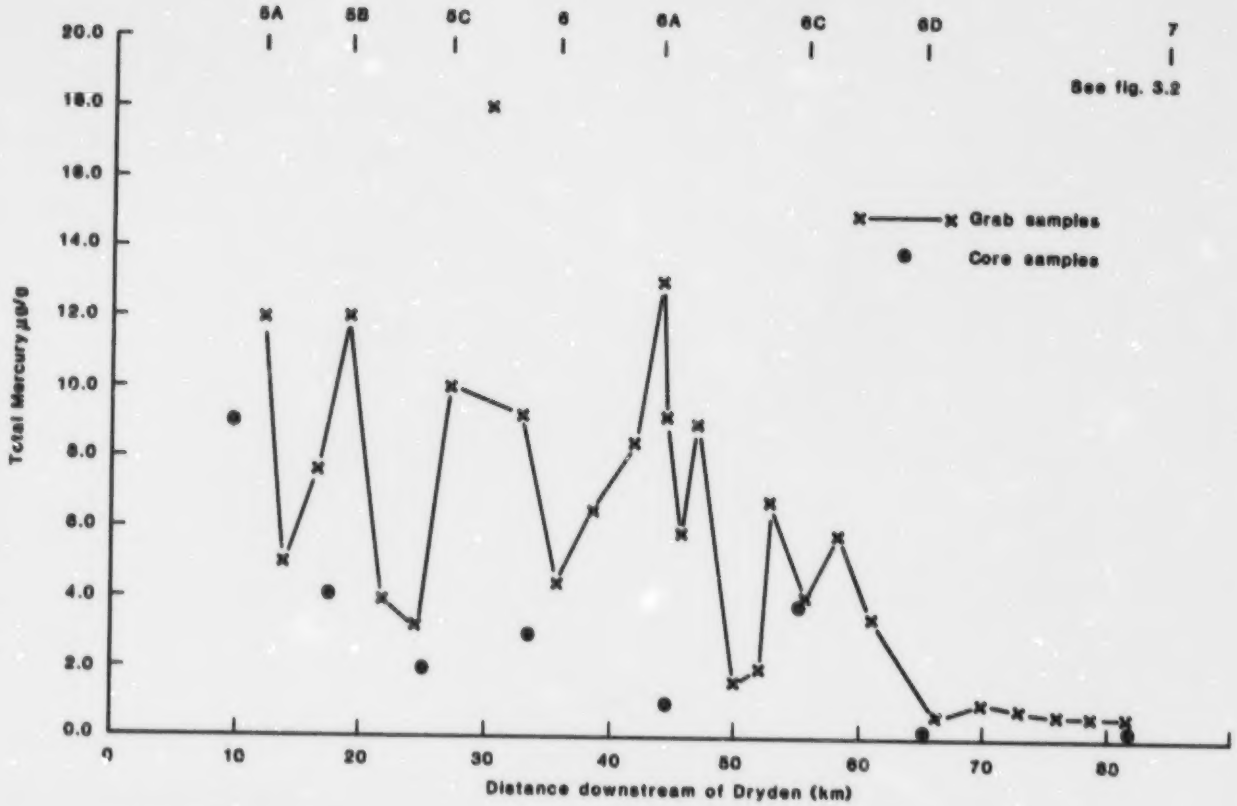

Figure 3.9 Mercury concentrations in surface sediments of the Wabigoon River from Dryden to Clay Lake 1980

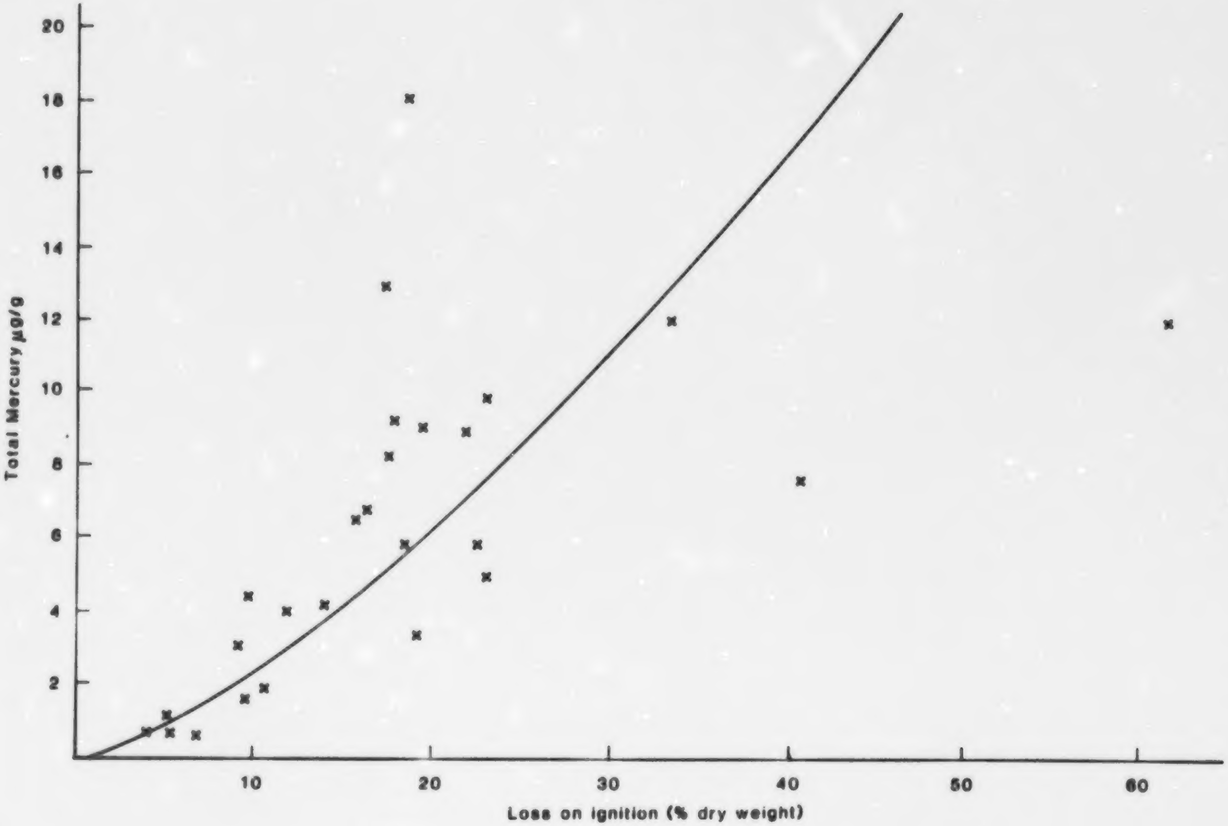

Figure 3.10 Relationship between Total Mercury and organic matter (as loss on ignition) for sediments in the Wabigoon River Dryden-Clay L. $r = .86$ $p < .001$

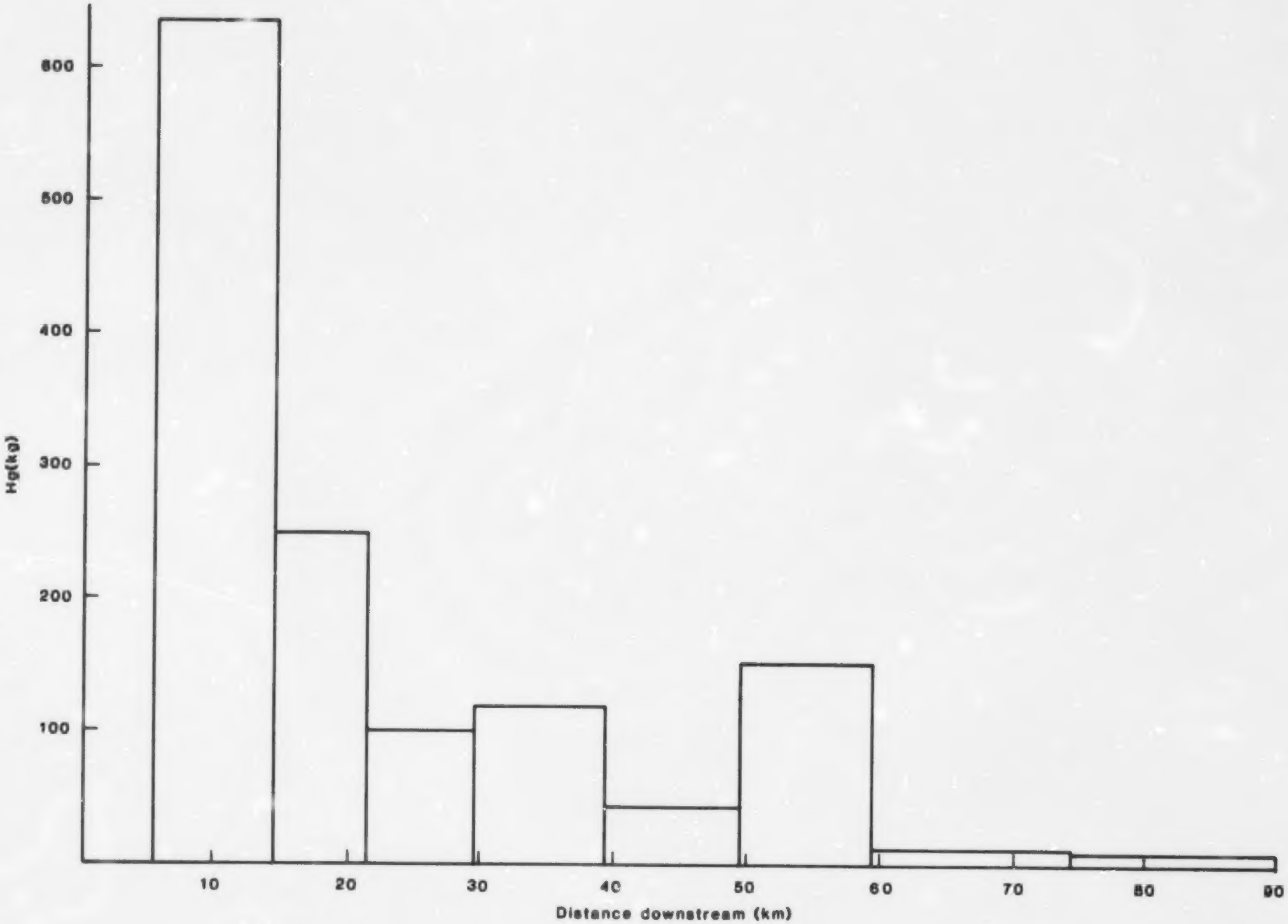

Figure 3.11 Estimated quantity of anthropogenic mercury in Wabigoon River sediments between Wainwright Dam and the inlet to Clay Lake.

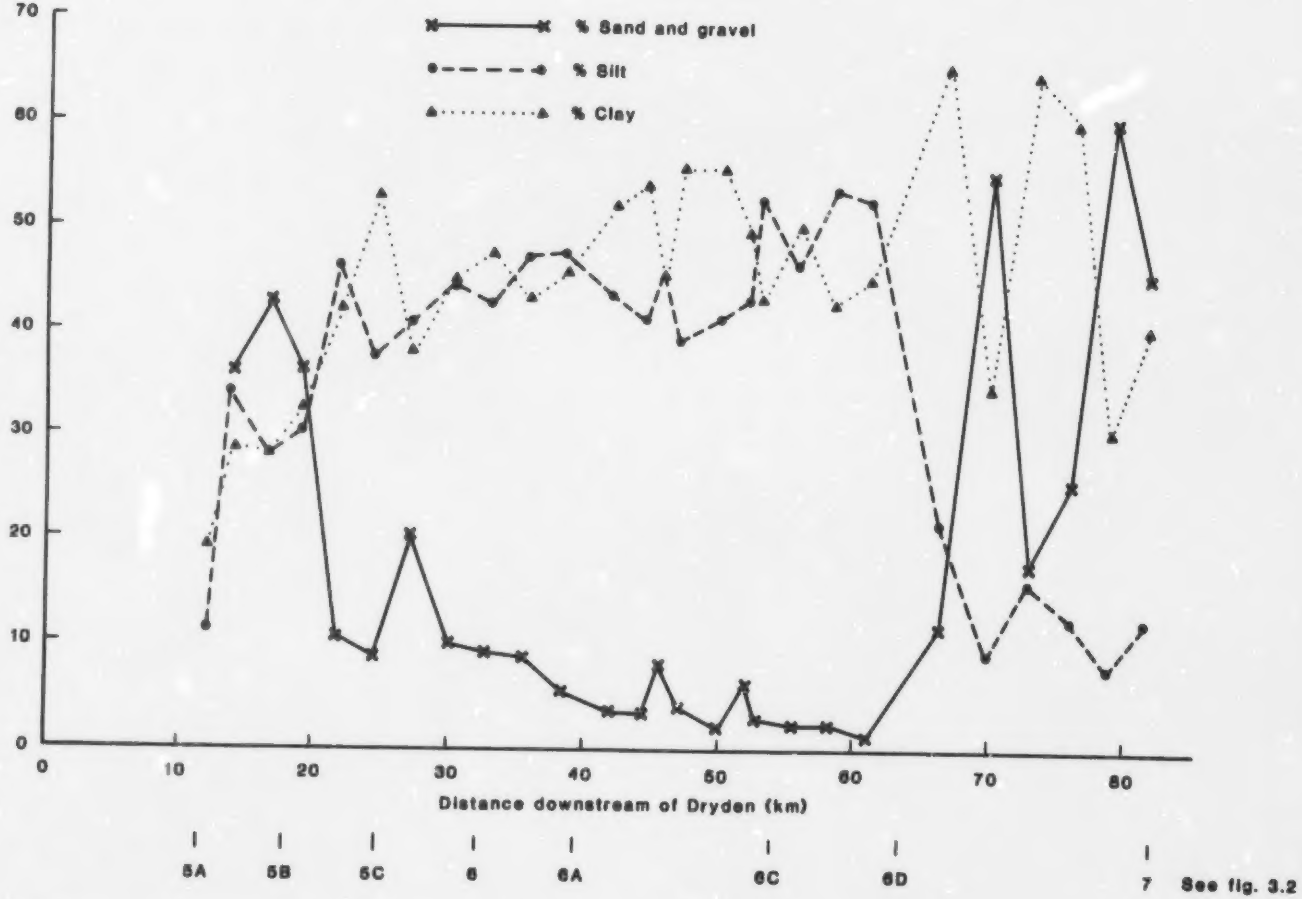

Figure 3.12 Particle size of sediments in the Wabigoon River from Dryden to Clay Lake 1980

4. TOTAL AND METHYLMERCURY IN WATER

4.1 INTRODUCTION

Mercury may be converted from organic to inorganic forms and vice versa in aquatic systems (Miller, 1977; Beijer and Jernelov, 1979). This section of the report documents methylmercury and total mercury concentrations in waters within the study area. Where possible, cause and effect relationships to explain field observations are derived, using basic water quality and hydrologic parameters (Section 2). Methylmercury concentrations in water play a major role in determining mercury levels in fish (see Section 5). In addition to understanding mercury dynamics, (changes in the form and concentration of mercury), we studied the geographical movement of total and methylmercury and calculated loadings.

The following comments briefly review water and sediment features affecting mercury levels and movement in the aquatic environment. For more information on the biogeochemistry of mercury, the reader is referred to several reviews (Nriagu, 1979; Miller, 1977).

Natural waters are complex systems containing organic and inorganic matter in dissolved, colloidal and suspended states. Interactions between ion-ion, ion-solid, and water-solid phases can play key roles in the distribution and transport of mercury between the solid and aqueous phases. Most mercury in the aquatic environment is bound to other molecules: the binding strengths range from weak Van der Waals forces to strong covalent complexes or chelates. The absolute quantities of mercury in these chemical forms are dependent upon the pH, Eh (reduction-oxidation potential), the type and concentration of the inorganic and organic constituents and chelating agents. All these factors vary in natural environments and must be considered in determining cause and effect relationships governing mercury levels.

Binding of mercury in sediments is influenced by reducing conditions. A strong and well defined Eh gradient usually exists at the sediment-water interface when surface waters are aerobic. This gradient can play a vital role in limiting sediment-water exchange processes (Hutchinson, 1957). In the absence of bioturbation (physical mixing of sediments by bottom dwelling organisms), it is possible that only the top few millimetres of sediment play a major role in the aquatic mercury cycle.

(a) Inorganic Chemistry - Eh-pH Diagrams

An Eh-pH diagram (Figure 4.1) describes mercury in various oxidation states and mercury compounds in an aqueous environment, and represents thermodynamically stable species at equilibrium. Organic compounds, which play a key role in the mercury cycle in natural waters, are neglected.

Depending on the value of Eh, mercury can be present in three oxidation states: elemental (Hg^0), mercurous (Hg^+), or mercuric (Hg^{++}). In nature, the Eh range is approximately -0.5 to +0.5 volts. Most aerated, surface waters have a potential of about +0.5 volts. The pH ranges from about five to nine. Therefore, mercury liquid and mercury sulphide will be the prime species affecting mercury solubility.

Figure 4.2 shows the influence on mercury solubility of chloride and sulphate, both of which are common in surface waters. Only the main soluble species are shown: those with a mercury concentration greater than 5 µg/ℓ (micrograms of mercury per litre of water). According to Gavis and Ferguson (1972), ammonia, carbonate, bicarbonate, and phosphate ions in natural waters do not affect the relationships shown in the diagram. The fields of mercury chloride complexes shrink with lower chloride concentrations, but the mercuric sulphide field stays approximately the same over the range of sulphide ion concentrations found in nature. In well-oxygenated alkaline waters, the solubility of mercury increases with the formation of mercuric hydroxide ($Hg\ (OH)_2$). In chloride-rich acidic waters, increases in solubility are the result of the formation of complexes of mercuric chloride ($HgCl_2$) and $(HgCl_4)^{2-}$. Since most surface waters have potentials of approximately +0.5 volts, the chief inorganic soluble species in natural waters will be mercury ions in solution and mercury-chloride/mercury-hydroxide complexes. This interpretation agrees with work conducted by Hahne and Kroontje (1973). Under reducing conditions in sediment, the presence of free sulphide should, in theory, effectively sequester inorganic mercury by the formation of mercuric sulphide, regardless of the chemical state of the mercury when it enters the sediment.

A slight reduction in the Eh field would result in the predominance of aqueous elemental mercury, which has a very high vapour pressure. This may be the reason that several laboratory studies have documented mercury losses to the atmosphere from the water column (Ramamoorthy, 1983; Bisogni and Lawrence, 1975; Spangler, et al., 1973).

(b) Organic Chemistry - Methyl and Dimethyl Mercury

The significance of methylmercury was first shown by Westoo (1966), who found that this form of mercury occurred in fish regardless of whether the source of mercury contamination in the area was phenylmercury, methoxymethyl mercury or methylmercury. Monomethyl mercury (CH_3Hg^+), is a substituted salt and is reasonably water soluble. Dimethyl mercury (CH_3HgCH_3) remains undissociated in solutions and is much less soluble than the monomethyl form.

The presence of methylmercury compounds in natural waters was unexpected as there was no apparent pathway for its formation. Jenson and Jernolov (1969), however, showed that methylmercury could be synthesized from inorganic mercury in sediments, probably through biological mediation. Many laboratory studies have shown that methylmercury compounds can be produced under a wide variety of common environmental conditions. Several mechanisms for the formation of methylmercury have been suggested (Bisogni, 1979), but it is not understood which processes dominate in specific conditions. Factors affecting methylation rates in sediments include pH, Eh, bacterial species, organic content, temperature, and mercury species and their concentrations. Generally, increases in bacterial populations result in higher rates of methylmercury formation. Increases in temperature and organic matter produce the same result, probably through stimulation of microbial activity.

Acidic conditions favour monomethyl mercury compounds while an alkaline environment promotes dimethyl mercury formation. In the presence of sulphide ion (low reducing potential), mercury concentrations are probably too low to be utilized by bacteria. However, when sulphide oxidizes to sulphate, the mercury is converted to a soluble form and becomes more available for methylation. According to Fagerstrom and Jernelov (1971), methylation of mercury from mercury sulphide can occur, but the rate is about 1,000 times slower than that when divalent mercury is present. Olsen and Cooper (1974), however, reported higher methylmercury formation under reducing conditions. The effect of Eh is unclear, but highly organic sediments producing large amounts of hydrogen sulphide will evolve dimethyl mercury from methylmercury (Craig and Bartlet, 1978). Besides forming methylmercury compounds, certain bacteria may degrade organic mercury to hydrocarbons and inorganic mercury (Beijer and Jernelov, 1979). The observed production of methylmercury is the net rather than the gross methylation rate.

Certain fungi are capable of methylating mercury from inorganic forms. The formation of organic mercuric compounds through this process may be significant (Beijer and Jernelov, 1979).

A steady-state (concentrations stable with time for a given set of environmental conditions) in sediments appears to exist between methylmercury and other forms. Therefore, more methylmercury may be produced in a flowing system than a static one (Kudo, et al., 1980; Miller, 1977). In rivers, methylmercury in overlying waters is carried away as it is released from the sediment.

The chemistry of mercury is closely linked with sulphur, oxygen, and hydrogen, the same elements that are associated with biological processes. Biological material contains much higher levels of sulphydryl (R-SH) compounds than the surrounding waters. The high affinity of these sulphur compounds for methylmercury is largely responsible for high mercury levels in fish. Divalent mercury has a very high affinity for a large number of organic substances, especially proteinaceous materials containing the sulphydryl group. Reimers, et al. (1974) concluded that all forms of particulate organic matter absorbed inorganic mercury, but only sulphur-containing organics had an absorption capacity greater than that for clay and sand.

In natural waters, mercury may be associated with suspended solids. The strength of the mercury-particulate bond affects its bioavailability. If mercury is incorporated into the mineral lattice, it becomes inert. Under oxidizing conditions, mercury may also be adsorbed onto iron-manganese hydroxides and be released again in a reducing environment. Mercury can be bound to plankton or washed from the watershed with detritus.

Suspended solids are usually defined as particles retained by a 0.45 micron filter. However, this definition is arbitrary and variable fractions of the finest colloidal material may be retained. In the Wabigoon River system, colloidal lacustrine clay may be important in the partitioning and transport of mercury. Such particles have a large surface area in relation to their weight.

4.2 SELECTION OF STUDY SITES

For the first year of this study, sampling sites were located from Dryden to the outflow of Clay Lake (Figure 4.3). The control site (site 1), at the outflow of Wabigoon Lake, is upstream of any known industrial discharge. Site 3 comprises effluent from Great Lakes Forest Products Limited. Sites 4 and 5, at the inflow and outflow of Wainwright reservoir, were established to determine the effect of the reservoir on mercury mobility and form. Sites 7 to 10 monitored Clay Lake at its inlet, eastern and western basins, and outlet. Due to unsafe access, spring sampling at site 7 was carried out at Quibell Falls, 13 km upstream.

In the second year, another river site was established at Minnitaki (site 6), plus a control site at Eagle River (site 2). Monitoring sites were added at sites between Clay Lake and the Manitoba border to assess the effects of large influxes of clean water. Ball Lake was sampled at the English River inflow (site 12), at the contaminated Wabigoon River inflow (site 11), and at the Ball Lake outflow (site 13). Sites at Sand Lake, Umfreville Lake and Eaglenest Lake were also included in the second year of the program to assess the effects of the Winnipeg River. Lount Lake (site 14) was incorporated to provide information on the English River system at a point midway between the Wabigoon River inflow and the Winnipeg River junction.

4.3 TOTAL MERCURY

(a) Study methods

1. Sampling

(i) 1978-79

During the ice-free season, weekly duplicate water samples were obtained at midstream with an acrylic "Van Dorn" or "Kemmerer" sampler. Winter samples were collected monthly. With the exception of site 9, all sites were sampled at a depth of 1 metre. At site 9, monthly samples were collected at depths of 1, 4, 7, 10, 13, 16 and 19 metres. In addition, duplicate weekly composite samples were taken from the epiliminion, metalimnion and hypolimnion at site 9. These zones were determined by temperature profiles obtained with a "YSI" telethermometer before sampling. Each composite sample was composed of a sample taken at the top, middle and bottom of each limnetic zone.

In August, 1978, we carried out an investigation at site 4, the inflow to the Wainwright reservoir, to formulate river sampling strategy. We sampled at 10 percent increments across the river with a U.S.H.D., model 49, depth-integrating, suspended-sediment sampler. Flow velocities were obtained using an Ott Universal Current Meter, model C-31. Duplicate filtrates of samples passed through a 0.45 micron Millipore filter were also obtained. Vertical fixed-depth sampling was conducted at midstream.

Cross-sectional sampling showed that mercury levels were not related to water velocity (Figure 4.4). Just under half the mercury was associated with particulate matter (Table 4.1). The inverse relationship between particle size and mercury concentration (Armstrong and Hamilton, 1973; Rust, 1977) indicates that much of the mercury may be bound to small particles, the distribution of which does not depend on water velocity or sampling depth (Ongley, 1977). Data from samples at different midstream depths (Table 4.2) confirmed that mercury levels were not related to depth below the surface. Thus, for typical flows which prevail for more than 90 percent of the year, mercury concentrations were relatively uniform throughout the water column. Also, any mercury loadings from Great Lakes Forest Products Limited are either negligible or are well mixed in the receiving stream by the time they reach site 4.

Bed sediment transport studies were not conducted. Bed sediment translocation, which probably occurs during high flows in the spring, probably has negligible impact on uptake by biota, but could have a long-term effect on mercury methylation where the sediment is deposited. Midstream subsurface sampling was deemed adequate for our study, but it might have led to underestimates of mercury loadings at some sites during high flows.

Samples from the effluent from Great Lakes Forest Products Limited were collected jointly by Ministry of the Environment and company staff using an "Isco" composite sampler. Samples of the total pulp and paper mill effluent were collected every 20 minutes in a 10-litre plastic container which was emptied daily. A possible shortcoming in this method was that some of the samples were 24 hours old before acidification. Another "Isco" was installed to permit immediate sample preservation: parallel samples in duplicate from each unit were procured thereafter for 10 days. For 20 tests for each sampler, there was no statistically significant difference between methodologies and immediate sample preservation was discontinued. Although sampling frequency was usually weekly, daily samples were also collected for a 10-day period to determine daily variability in mercury levels.

The Eagle River was sampled 26 times. Four other uncontaminated tributaries of the Wabigoon River - Buller, Rugby, Hutchison and Aubrey Creeks - were sampled three times during the study period to measure the natural loadings to the Wabigoon River and Clay Lake. Five grab samples were also obtained from the outflow of the Dryden sewage treatment plant, which utilizes secondary treatment.

During spring flows, sampling frequency on the river was increased. Samples were often taken twice a day during the rising limb of the hydrograph. Daily mercury concentrations were determined during the spring runoff and, where necessary, data were interpolated to calculate the monthly average. Mean annual concentrations of mercury were derived from average monthly values.

(ii) 1979-80

Sampling for sites 1-10 was unchanged from the first year of the study. All new sites were sampled at a depth of 1 metre and at an initial frequency of once monthly, beginning in July, 1979. After the results of the first four months were available, all new sites except Ball Lake were abandoned. Many of the mercury values were below detection limit at the other downstream sites, and continued sampling was considered unnecessary.

2. Centrifuge Study

A joint study of suspended sediment was undertaken between the Ontario Ministry of the Environment and the National Water Research Institute, Western Region, using a field centrifuge. Suspended sediment was obtained during different seasons at sites 1, 2, 3, 4, 5, 7 and 10 following methodology described by Jackson et al. (1983). Suspended particulate matter was subjected to a progression of increasingly strong leaching solutions to determine the strength of bonding between mercury and particles. Water samples for mercury analysis were collected at the influent and effluent of the centrifuge. Results of this study are presented in Jackson, et al. (1983), and only selected data will be discussed in this section of the report.

3. Loading Calculations

Mercury budgets were derived from mercury concentrations and daily flow data supplied by the Water Survey of Canada and Great Lakes Forest Products Limited (see Section 2). Since industrial effluent was not included in recorded flows for the Wabigoon River at Dryden, a mean effluent flow of 1.6 m^3/s was added to discharges at stations 4 and 5.

To determine the water inflow to Clay Lake, discharges at Quibell were prorated. Since most of the flows in the watershed are controlled by dams, unregulated runoff was used to estimate flow increments between Quibell and Clay Lake. Flow rates were determined from the following equations:

$Q_{QCL} = 0.12\ Q_U$

$Q_U = Q_Q - (Q_{WD} + Q_{ER})$

where:

Q_{QCL} = unregulated runoff to Wabigoon River between Quibell and Clay Lake
Q_U = unregulated runoff upstream of Quibell
Q_Q = Wabigoon River discharge at Quibell
Q_{WD} = Wabigoon River discharge at Dryden (regulated flow from Wabigoon Lake)
Q_{ER} = Eagle River discharge (regulated flow from Eagle Lake)

Similarly, flows were prorated at other downstream sites from the nearest hydrometric station.

The mean monthly water outflow of Clay Lake was assumed to equal the inflow. The error in this assumption is thought to be no more than 10 percent for spring flows, and a maximum of 5 percent at other times. The theoretical residence time is only 2 months, based on the mean annual flow, and runoff from the Clay Lake drainage basin is small. We also assumed that the mean monthly outflow of Ball Lake is equal to the combined inflows of the Wabigoon and English Rivers.

4. Analytical Methods

Organo mercury compounds in water are oxidized to inorganic forms by heating the sample in a mixture of sulphuric acid, potassium permanganate and potassium persulphate. After oxidation takes place, the mercuric compounds are reduced with stanrous sulphate in a hydroxylamine sulphate - sodium chloride solution. The mercury is sparged from the solution with a stream of nitrogen and is trapped on silver. The silver is heated and the released mercury is flushed with nitrogen through an absorption cell situated in the light path of a mercury lamp. The absorption is read at 253.7 nm (nanometres). The detection limit of the method is 5 ng/ℓ (nanograms of mercury per litre of water) for a 150 ml sample (Furutani and Rudd, 1980).

(b) Results and Discussion

1. Data Integrity

All samples were collected in duplicate and we present the means. For means from each site, the average standard deviation was calculated (Table 4.3). The variability associated with field collection and laboratory analysis (1.8-7.2 ng/ℓ) was generally no greater than the laboratory precision (5 ng/ℓ). The percentages of samples with concentrations above the laboratory detection limit of 5 ng/ℓ are also given in Table 4.3. Results which were below detection limits were assigned values of 2.5 ng/ℓ for computational purposes.

2. Geographical Trends

Mean concentrations for the second study year are presented in Tables 4.4 and 4.5. Results for four months sampling of the entire river system are presented in Table 4.6. Section 4.5 discusses results from a special survey in late 1980.

Table 4.4 shows that all monitoring sites had higher mercury concentrations than control sites at Wabigoon Lake, Eagle River, and the English River inflow to Ball Lake. Average mercury values for sites 4 to 8 (Wainwright Dam to the eastern basin of Clay Lake) ranged from 24 to 29 ng/ℓ, compared with 3 to 5 ng/ℓ for controls. Mean mercury concentrations were 16 ng/ℓ at the western basin of Clay Lake, and 19 ng/ℓ at its outflow. Concentrations at the inflow to Ball Lake (site 11), approximately 40 km downstream of Clay Lake, were similar to those at the western basin of Clay Lake. The average value of 8 ng/ℓ at the English River outflow of Ball Lake (site 13) was slightly higher than the English River (site 12) inflow value of 5 ng/ℓ, but the difference was not statistically significant. Mercury levels downstream of Ball Lake were also low (See also Table 4.6).

Nearly two-thirds of the mercury concentrations at the control sites were below detection limits. Mercury levels in other uncontaminated waters in the Wabigoon River watershed are presented in Table 4.7. Control values were lower than those for other shield waters in Canada. Kudo (1977) reported background values of 12 and 13 ng/ℓ for the Ottawa River, and Penn (1978) has found that waters in northwestern Quebec had mercury concentrations of about 10 ng/ℓ.

The mean annual mercury concentration in effluent from the Great Lakes Forest Products Limited mill was 194 ng/ℓ (Table 4.4). This value is typical of other pulp and paper mills, with or without chlor-alkali plants (Betts, 1980, Water Directorate, Environment Canada, personal communication). However, there is little information on loadings from pulp and paper complexes, because many laboratories cannot accurately determine low concentrations of mercury. Effluent sampling is fully discussed in Section 7.

A calculated mass balance shows that all the anthropogenic mercury in the water at the inflow to Wainwright Dam could have been derived from industrial effluent loadings. To determine the effect of effluent loadings, mercury concentrations at the Wainwright Dam site were regressed against concentrations in a 24-hour composite sample of mill effluent. Under average flows, travel time to the Wainwright Dam is approximately

6 hours, and the theoretical residence time in the reservoir is approximately 3 hours. Weak, but statistically significant relationships, were found between mercury in mill effluent and mercury at Wainwright Dam (Figure 4.5).

Mercury concentrations at Minnitaki (site 6) and at the Clay Lake inflow (site 7) averaged 23 and 29 ng/ℓ respectively and are similar to values at site 4. The flows at site 7 are two to three times greater than those at Wainwright Dam. Therefore, additional mercury must have entered the water column between these sites, presumably by remobilization from contaminated sediments.

Mercury concentrations in the western basin of Clay Lake (site 9) averaged 16 ng/ℓ and were significantly ($p<.05$) lower than upstream values. Since concentrations at the outflow of Clay Lake (site 10) were only 66 percent of the inflow values, Clay Lake was a sink for some mercury entering in the Wabigoon River.

At the inflow to Ball Lake, about 150 km from the mill, mercury concentrations averaged 14 ng/ℓ. This level is 75 percent of the mean value at the Clay Lake outflow and about 50 percent of the mercury concentration immediately downstream of Dryden.

3. Temporal Trends

(i) Seasonal Variation

All total mercury data for sites 1-10 are presented in Figure 4.6. Although there were certain trend similarities between some sites, waters at each site are usually chemically different. Consequently, each site is discussed separately. Links between sites are noted. Since the effects of temperature and flow are closely related to season, the relationships between total mercury concentrations, temperature and flow were examined and are shown in Table 4.8.

Wabigoon Lake (Site 1)

Fifty-five percent of the values were below detection limit and are plotted as 2.5 ng/ℓ in Figure 4.6. In the first study year, there were summer and winter maxima. Concentrations thereafter were generally low until another peak was recorded in June, 1980. This last peak had the highest value (36 ng/ℓ) for the entire study, although similar values were found in August and September, 1980 (Section 4.5), after the joint federal-provincial study had concluded. These high values may be related to drought conditions. During spring runoff, in late April, concentrations of mercury were moderately elevated.

Eagle River (Site 2)

As 71 percent of the concentrations were below detection limit at this site, temporal trends are difficult to define. As found for Wabigoon Lake, total mercury concentrations at Eagle River were substantially elevated, for unknown reasons, during the drought in 1980 (Section 4.5).

Great Lakes Forest Products Limited (Site 3)

Temporal trends for effluent from Great Lakes Forest Products Limited are difficult to discern because of the sampling frequency. The variation in mercury in effluent samples is also large. Concentrations at the end of the study period were, however, substantially lower than at the start. See Section 7 for further discussion.

Inflow to Wainwright Dam (Site 4)

During non-high flows, mercury at site 4 fluctuated randomly with no relationship to flow or temperature (Table 4.8). During the regulated high flow in May, 1979, mercury concentrations increased by more than an order of magnitude (Figure 4.7). Highest mercury levels were recorded just before maximum flow. This phenomenon is common for sediment-bound contaminants eroded during high-flow events. The data also suggest that threshold flows for moving maximum quantities of mercury are in the 50-70 m^3/s range. When all data for high flow events are pooled, it is clear that sediment exhaustion occurs very quickly, thus accounting for the poor relationship between mercury concentrations and flow.

Outflow of Wainwright Dam (Site 5)

Total mercury concentrations at the Wainwright Dam outflow were similar to values at the inflow during non-high flow events. No trends were apparent. During the first study year, concentrations at both sites decreased from August, 1978 to March, 1979 (Figure 4.6). The relationship between temperature and mercury level at this site was very weak, but still statistically significant. The effects of the regulated high flow in May, 1979, on mercury levels at site 5 were similar to those observed at site 4 (Figure 4.7).

Minnitaki (Site 6)

Here, mercury concentrations fluctuated randomly throughout the study. Highest values occurred in June, 1980, under low flow conditions. There was a negative correlation between mercury concentration and flow at this site (Table 4.8).

During the high regulated flows in May, 1979, mercury concentrations paralleled those of the two upstream sites, with a maximum concentration of 725 ng/ℓ. Hydrological records are not available for this site, but the flood levels during the natural spring runoff in April, 1979 were similar to those of the elevated discharges in May. Concentrations during the unregulated spring runoff averaged 20±6 ng/ℓ for 20 samples. The uncontrolled spring runoff entered the river below Wainwright Dam in April, while the regulated flow entered above the dam in May. Sediment resuspension resulting from these different flow sources gave greatly different results for mercury concentrations.

Inflow to Clay Lake (Site 7)

At this site, there were definite summer maxima and winter minima (Figure 4.6). Excluding effects of spring runoff, mercury concentrations were related to water temperature (Figure 4.8). This strong relationship has not been reported elsewhere in the literature. The transfer of mercury from bed sediments to overlying waters involves diffusion, microbial oxidation of mercury-rich organic detritus and the activity of bottom-dwelling fauna. Diffusion rates are affected by temperature but likely vary by a factor of only 1.5 to 2.0 over the 20°C temperature range observed in the field (R. C. Aller, 1977). In a study of mercury losses from sediments similar to those in the Wabigoon River (i.e.: a mixture of wood wastes and silt), Boddington et al. (1979), found that the rate of release of mercury was positively correlated with the number of tubificid oligochaete worms. Thus, the predominant processes responsible for substantially elevating mercury levels in water are probably biological.

The effects of temperature and flow on mercury concentrations during high flow events are shown in Figures 4.9-4.11. In 1978 and 1979, twin flow peaks were recorded. The first peak was caused by natural runoff entering below Wainwright Dam, and the second was mostly due to water released from Wabigoon Lake. Higher mercury concentrations were associated with the second less intense, spring peak in both years. The regulated peak in 1979 from the spill at Dryden had a greater impact on bed sediments near the head of the study area, where mercury concentrations in sediments are highest. Mercury concentrations at the inflow to Clay Lake during the regulated flood, while elevated, were much less than the peak values at Minnitaki and at Wainwright Dam. Since dilution from incoming clean flows cannot fully account for the substantial decrease, much mercury must have been removed from the water column between Minnitaki and the inflow to Clay Lake. This process is discussed under loadings (page 17). In 1980, the mercury peak during the runoff was about 50 percent of the other spring peaks. Consequently, while a good portion of the spring mercury influx in 1978 and 1979 was probably sediment-associated, there may have been proportionately less entering Clay Lake in this form in 1980. Excluding high flow events, there is a significant negative correlation between mercury concentration and flow (Figure 4.12).

Clay Lake, Eastern Basin (Site 8)

In the eastern basin of Clay Lake, strong seasonal trends are also evident. Maxima during summer and fall, and minima during winter were more than an order of magnitude different. Temperature had a major effect on mercury levels at this site (Figure 4.13). However, in 1979, the highest mercury values were recorded after temperatures dropped sharply in the fall. Mercury levels were probably influenced by the population of algae, since algae are known to be accumulators of mercury. Even without the phytoplankton implications, temperature-related effects could account for most of the variability.

During the study period, there were two atypical peak concentrations: one of 103± 5.7 ng/ℓ in October, 1978, and one of 100±0 ng/ℓ in May, 1980. It is possible that one or both of these peaks are related to industrial operations at Dryden. Mercury concentrations were 900 to 970 ng/ℓ in the industrial effluent 1 week before the detection of high mercury levels in October, 1978, at Clay Lake. Those levels were the highest detected during the study year and were three times higher than the mean of all samples from the mill. Because effluent sampling was carried out weekly in October, 1978, a mercury "spike" may have passed down the river without being detected at sampling sites. The federal research team reported high mortality of minnows in a caging experiment at site 7, during the same week that elevated mercury levels were detected at site 8. Since the recorded mercury levels should not have been fatal, other water quality characteristics were probably also influenced at the time of the increase in mercury concentrations. Our data suggest that mercury levels in the eastern basin of Clay Lake may have been affected by either high mercury concentrations in mill effluent and/or chemicals in the industrial effluent capable of extracting mercury from bed sediments.

Clay Lake, Western Basin (Site 9)

At the western end of Clay Lake, seasonal effects are clearly evident, though less dramatic than those at site 7. The effect of temperature on mercury levels at this site is shown in Figure 4.14. Maximum mercury values occurred in the summer and fall. Because surface values are also affected by internal lake cycling, mercury concentrations in the late fall are higher than most values at upstream sites. The lag in increase in the early summer suggests that mercury concentrations at this site may be affected by upstream loadings.

Vertical profiles of mercury concentrations in the western basin of Clay Lake for the first study year are presented in Figure 4.15. Trends in the first year were repeated in the second year (Table 4.9). In the hypolimnion, there are two distinct peaks in mercury concentration, (Figure 4.16). The peaks are separated by the fall turnover when mercury levels and water temperature in the entire water column are the same (Figure 4.17). During stratification, mercury levels increased near the lake bottom as summer progressed (Figures 4.18 and 4.19) and dissolved oxygen fell to zero (Figure 4.20). Maximum mercury values in 1978 occurred in August, just before turnover. After a temporary decrease at fall turnover, mercury levels again rose near the lake bottom, decreased steadily through the winter and spring, and reached a minimum in June, 1979. Maximum mercury levels during the summer of 1979 were approximately half the concentrations recorded in 1978. Neither anoxic conditions in late winter (Figure 4.20), nor the spring turnover had any effect on the rate of decrease. These fluctuations could not be explained by the normal chemical and physical changes in a dimictic (stratified) system. For example, in the summer, elevated mercury levels could be related to the resolubilization of mercury co-precipitated with iron or manganese oxides. However, during late winter, mercury levels steadily decreased during anoxic conditions. This decrease indicates either that these oxides do not have an appreciable role in the cycling of mercury, or that mercury is desorbed from the oxides and rapidly re-precipitated as a sulphide. Although sulphide levels were below the detection limit, some sulphide must be present in water since it is found in sediments. Theoretically, the formation of mercuric sulphide complexes should precede those with iron sulphide.

Mercury levels in the hypolimnion (Figure 4.15) in the first half of the calendar year did not increase under either anoxic conditions (in February, March, April), or oxic conditions (in May, June). Therefore, we believe that a steady rate of mercury release from sediments is of minor significance in the western basin. Elevated mercury levels in summer are probably the result of mercury "raining out" (deposition of mercury in phytoplankton and other suspended particulate matter). If most of the mercury in the rainout was associated with phytoplankton, the temporal pattern in mercury in water near the lake bottom could be explained. The strong relationship between total mercury and suspended nitrogen for samples collected one metre off bottom supports this interpretation (Figure 4.21). Mercury sequestered by algae during summer blooms would either be recycled in the upper waters or become trapped in the hypolimnion, depending on the decomposition rate of the algae. Since algae are most plentiful in summer, mercury levels associated with suspended algae in the hypolimnion would also be much higher in summer than in winter. Because the heaviest blooms occur in July and August, mercury accumulation in deep water in May and June would not be expected. This is precisely the situation observed in Clay Lake.

Clay Lake Outflow (Site 10)

At the outflow of Clay Lake, there were summer maxima in the total mercury concentration in both years, but the winter minimum was not as pronounced in 1979 (Figure 4.22). The direct effects of temperature play a less important role in mercury concentration here than at sites 7 and 8. The effects of internal lake cycling are greater at site 10 than at site 9. Mercury levels remained sharply elevated throughout the fall and winter of 1979-80, in contrast to all other sites. Mercury in the spring and summer of 1979 failed to correlate strongly with temperature. The lowest mercury concentration (2.5 ng/ℓ) at this site occurred on July 4, 1979, when water temperatures was 21°C, near its highest level for the year.

(ii) Inter-Year Comparisons

Mean total mercury concentrations for two, 12-month periods are presented in Table 4.10. Because there are results at many sites for only 23 months, data for the month of July, 1979, was incorporated into both data sets to compare the two, 12-month periods. The table shows that average mercury concentrations at contaminated sites were generally similar for both study years. Mercury levels in the Wabigoon River between Dryden and Clay Lake are also similar for both years, if the high flow data for May, 1979, are omitted.

Three years of results during ice-free months at Clay Lake are plotted in Figures 4.23 to 4.26. Mercury concentrations for 1978 and 1979 were similar. Concentrations in 1980 at some sites, however, were 50 to 100 percent above values in the previous 2 years. This phenomonon is most evident for the June-September period at the inflow to Clay Lake and for the May-September period at the outflow. The residence time for the ice-free period in 1980 is conservatively estimated as five times longer than that for the previous 2 years. Increased mercury levels may directly result from increased residence time, but other water chemistry factors affecting mercury concentration, such as pH, chloride, suspended solids, or algae may also be involved (Ontario Ministry of the Environment, unpublished data).

Seasonal variations in mean mercury concentrations for Clay Lake, based on data from the western basin, are illustrated in Figure 4.27. These concentrations exhibit the same recurring patterns observed at surface sites. Mercury levels usually ranged from 9 ng/ℓ in late winter to 23 ng/ℓ in the late summer and fall. Mean concentrations for the first year were 17.3 ng/ℓ, slightly higher than the average of 14.9 ng/ℓ for the second year. The difference was primarily due to the sharp difference between August and September values in the 2 years. Mercury levels in the epilimnion, metalimnion and hypolimnion for both years are plotted in Figures 4.25, 4.28 and 4.29, respectively. Mercury concentrations were clearly lower in the summer of the second study year, particularly in deep water.

4. Form of Mercury in Water

Many investigators (Armstrong and Hamilton, 1973; Hinkle and Learned, 1969; Cranston and Buckley, 1972) believe that mercury in freshwater is usually attached to particles. In our study, "soluble" and "bound" mercury were separated with a field centrifuge. Summaries of total mercury concentrations in suspended and soluble phases for different seasons are presented in Figure 4.30 and Table 4.11, respectively. Figure 4.30 shows that mercury concentrations in suspended particles are elevated at all sites compared to controls, following the trend shown for total mercury in soluble and bound phases combined (Table 4.4).

April samples were collected during the rising flow of the uncontrolled runoff in 1979 (Figure 4.10) while May samples were obtained during the rising hydrograph for the regulated flood at Dryden. The second flood had a much greater effect on suspended particulate mercury levels in the Upper Wabigoon River than the first. At Wainwright

Dam and Minnitaki, mercury-enriched sediments were resuspended during the second flood when flows were highest at the upper end of the system (Figure 2.6). During low flows in July and August, when there was little suspended matter, mercury concentrations on particulate matter were very similar at all sites. During non-high flows, mercury is partitioned between the "free" and "bound" forms, as shown in Figure 4.32. Such partitioning likely develops quickly; within hours or days (Rudd, et al., 1980).

A further discussion of mercury chemistry and cycling can be found in Section 4.6.

5. Steady-State Considerations

We considered whether mercury concentrations in the Wabigoon system could be described as being in steady-state with other components of the ecosystem. Steady-state implies a balance between mercury inputs and outputs in the water column at any given site in the system. We also considered the kinetics involved in reaching this steady-state condition.

Usually, bed sediment contains well over 95 percent of the mercury in the system and is the primary source of elevated mercury concentrations. We believe that a steady-state exists between mercury in the water column and mercury in bed sediments, at least in parts of the system.

A 10-week intensive sampling survey (Section 4.5) revealed that mean mercury levels were very similar at all sites, although water flows increased downstream. Mean levels of mercury downstream of the Eagle River confluence (58 ng/ℓ) were even slightly higher than the upstream values of 50 ng/ℓ, despite the influx of the Eagle River with a mercury level of 15 ng/ℓ. Contaminated sediments appeared to add mercury rapidly to the clean water inflow. The sites upstream and downstream of the confluence are 3.6 km apart. Once steady-state conditions were achieved, the time of contact between water and sediment did not affect mercury levels. Mercury concentrations in water did not increase in the river at sites further downstream or in the eastern basin of Clay Lake. Mercury levels at the inflow to Clay Lake and in the eastern basin were virtually identical at 61 ng/ℓ.

The effects of residence time in the river or lake are discussed in Section 4.5. With up to 10 fold increases in residence time, mercury concentrations increased by a factor of approximately 1.5.

Further evidence of the partitioning of mercury (separation of mercury into different forms or between different components of an ecosystem) in sediment and water is shown by comparing trends of mercury in water at four sites: the inflow to Clay Lake, the eastern basin, and two control "tubes" used by Rudd, et al. (1980) in the eastern basin of Clay Lake. The walls of the tubes in Rudd's study were sealed into the lake sediment to prevent exchange of mercury between lake water inside and outside the tubes. The parallel trends in mercury levels over a 9-week period at the four sites

(Figure 4.33) indicate that the same factors affected mercury levels in water inside and outside the tubes. We concluded that mercury levels in the tubes were derived from the lake sediment. These results imply that concentrations in Clay Lake waters could be driven by Clay Lake sediments alone, in the absence of any mercury loadings from the Wabigoon River.

When residence time does not affect mercury concentrations, the system is considered to be at steady-state. That is, for any given location and set of environmental conditions, mercury entering by transport in the water column and mercury released from sediments into overlying waters is balanced by losses through the water column and to the atmosphere. Steady-state also implies no change in concentration throughout the year. In this contaminated system, however, seasonal fluctuations in mercury concentrations in the water column are large in response to temperature and flow variations. We suggest the term "dynamic steady-state" to describe this condition. To test this hypothesis, concentrations of total mercury in similar sediments and water at several sites were plotted in Figure 4.34. Caution must be exercised in interpreting this relationship because factors controlling mercury concentrations in waters in the control lakes are likely different from those in the most contaminated portion of the river system. Figure 4.34 suggests that there is indeed a relationship between mercury concentrations in sediments and waters although the form of the relationship is unclear. Studies in Clay Lake (Armstrong and Hamilton, 1973) and Ball Lake (Section 3) show that mercury concentrations in both basins, while significantly different from each other, are internally homogeneous. Cores collected from basin centres in the Wabigoon system provide good approximations of mercury concentrations for whole basins. All sediments used to develop this relationship were qualitatively similar and consisted of several millimetres of loosely compacted organic material overlying clay and silt. Improvement in the relationship shown in Figure 4.34 might be gained by taking particle size, organic content and dilution into account. Of course, in the longer term, mercury levels in water in the contaminated system are not at steady-state, but steadily decrease as mercury is lost from the active ecosystem through atmospheric and water column export and sedimentation.

Although we cannot quantify the kinetics in the sediment/water steady-state, evidence suggests that in this system, the process is complete within a few days. In the absence of a point source in Dryden, the rate could be calculated with time-of-travel, flow, wetted perimeter, and mercury concentrations during non-high flow periods. Even with a point source, however, average mercury levels at the inflow to Wainwright Dam were similar to values in the eastern basin of Clay Lake. Although this situation could be fortuitous, it suggests that steady-state concentrations of mercury were reached at site 4, less than a half-day in travel time downstream of Dryden under normal flows. The rapid response of mercury levels to temperature changes indicates that new steady-state conditions are achieved within a few days (Figure 4.8).

Steady-state kinetics were further examined in October, 1982, when mercury loadings at Dryden were reduced during a shutdown of the pulp and paper mill. We obtained water samples both before and during the shutdown period. A preliminary review of the data (unpublished) indicates that steady-state concentrations of mercury existed at Wainwright Dam in the absence of significant mill loadings.

6. Transport (Loadings)

(i) Geographical Trends

Transport of mercury through the system is greater than implied by its concentrations, since flow increases with distance downstream (Table 4.12). The normal background mercury loading at the outflow of Wabigoon Lake for the second year of the study was approximately 1 kg/year. At site 4, the first monitoring site downstream of the industrial discharge, the annual mercury loading increased to 7.4 kg. Contributions from pulp and paper mill effluents were about 9.7 kg. Loadings from the Dryden sewage treatment plant, the only other potential source, were not considered significant. Loading at site 5 was the same as site 4, which indicates that the Wainwright Dam and reservoir had little effect on total mercury loading. Loadings increased to 9.1 kg at Minnitaki and to 26.6 kg at the inflow to Clay Lake. These increased loadings result from increasing flow rates downstream, rather than changes in mercury concentrations. At the outflow of Clay Lake, the annual mercury flux decreased to 18.6 kg. Thus, about 30 percent of the mercury entering the lake was retained. The Wabigoon River discharged 18.9 kg of mercury into the English River. Loadings for the English River at the inflow and outflow of Ball Lake could not be calculated accurately. Since water has a low residence time in this lake, and since we found much less mercury in sediments from Ball Lake than Clay Lake, we believe little mercury settles out in Ball Lake. In any case, about 80 percent of the mercury leaving Ball Lake via the English River was from natural sources. At the outflow from Ball Lake, only about 14 kg of the annual mercury loading would have come from industrially related sources in the Wabigoon River. Most of the mercury discharged by the Wabigoon is from industrial sources (Figure 4.35). Natural loadings were calculated by multiplying the flow rates by background mercury concentrations measured at uncontaminated sites (Table 4.7). Each site in the Wabigoon River system has about the same percentage of anthropogenically derived mercury loading. These values range from 85 percent at site 7 to 71 percent at site 12.

(ii) Temporal Trends

Monthly mercury loadings for several sites are presented in Figure 4.36. The marked seasonal variation in concentrations recorded at some sites (Figure 4.6) is not evident in the loading values. The loadings are greatly influenced by flow. For example, the extremely low flows in May and June, 1980, resulted in some of the lowest monthly loadings recorded. Normally, spring loadings are highest. During May, 1979, the loadings at river sites increased more than the flow. This indicates that flow velocities in the river were high enough to induce sediment resuspension and transport.

Wabigoon Lake and Eagle River

At these control sites, flows are uniform and loadings directly reflect concentrations. Loadings were higher in the summer than in the winter. The relatively high loading at Wabigoon Lake in May, 1979, corresponded to a large release of water at Dryden following heavy rains. In 1980, flows at Dryden were reduced sharply because of drought and spring loadings were low that year. Loadings were also much lower at Eagle River in the spring of 1980 than in the same period the previous year.

Great Lakes Forest Products Limited

There were no seasonal trends for industrial loadings from this source.

Wainwright Dam

Loadings at the inflow and outflow were very similar. The lack of temporal trends is probably due to the effect of mill loadings. Because of low spring flows, loadings in 1980 were about a third less than those in 1979. In May, 1979, flood conditions were created by a controlled spill at Dryden. The effects of this increased flow on loadings at the inflow to Wainwright Dam are shown in Figure 4.37. In 7 days, 4.5 kg (30 percent of the total annual mercury loading) was recorded at this site. About 35 percent of the annual mercury flux at the outflow of the Wainwright Dam also took place during the same period. Because discharges at Great Lakes Forest Products Limited could have accounted for no more than 8 percent of this loading, most of it was ascribed to re-suspension of mercury-laden sediments. The centrifuge study also showed that mercury in the water samples at this time was almost entirely associated with particulate matter. Referring again to Figure 4.36, the similarity of monthly loadings at sites 4 and 5 over a wide range of hydrological and seasonal conditions is further evidence that the Wainwright Dam has no net effect on total mercury mobility.

Minnitaki

The highest monthly load of 10 kg occurred, as expected, during the controlled spring flood in May, 1979. This loading was about the same as the total of the other 11 months of the year. The effect of a controlled spring flush on mercury flux was greater than at upstream sites.

Clay Lake Inflow

Striking trends were evident at this site, where summer loadings were much greater than those in late winter. Mercury associated with resuspended particulate matter forms a portion of the total mercury flux during spring runoff at this site. In 1980, under low flows, there was little resuspension of sediments. An examination of the concentration data during the twin peak flows in 1979 indicates that mercury concentrations are highest during the second peak flow (Figure 4.10). The source of the first peak is unregulated runoff, while the second peak is caused by controlled discharge at Dryden (Figure 2.4).

Under typical conditions, resuspended mercury-enriched sediment accounts for 30-40 percent of the annual flux at Wainwright Dam and about 27 percent at the inflow to Clay Lake.

During a typical hydrological year (July, 1978 to June, 1979) 25 kg of industrially-produced mercury entered Clay Lake. A large reservoir of mercury-contaminated sediment remains in Wabigoon River sediment above Clay Lake. This may release large amounts of mercury to Clay Lake through sediment resuspension and transport. Figure 4.37 shows that, during high flows in May, 1979, more than 3 kg/day of mercury were being moved at Minnitaki. At Quibell, the loading was reduced by resettling to about 0.5 kg/day. These daily loadings correspond to 12 percent and 2 percent respectively of the annual loading to Clay Lake, and clearly show the potential for river bottom sediments to contaminate areas farther downstream.

Clay Lake Outflow

At this location, the loadings reflect the influence on mercury concentrations of processes within the lake. Loadings generally show similar fluctuations to those at the inflow. Peaks during spring runoff are moderated, presumably due to settling of particulate matter in the lake.

Anthropogenic mercury in the Wabigoon River may be derived from the following sources: 1) mill effluents, 2) leaching from contaminated bed sediment, 3) biological remobilization, and 4) re-suspension from bed sediment.

Figure 4.38 illustrates the relative contributions of these sources for the study year 1978-79. Biological processes were assumed to be related to temperature and leaching processes to elevated salt levels and depressed pH. During the 1980 drought year, the portion of the flux from eroded bed sediments was sharply reduced. Thus, the annual flux at Minnitaki could be reduced 50 percent by eliminating of controlled spring floods at Dryden. However, this change in water-level regulation would affect the use of Wabigoon Lake for cottagers and for power generation. The level of Wabigoon Lake would have to be raised 0.3-0.5 m to store the water released during the regulated floods in 1978 and 1979. Furthermore, in a typical hydrological year, flood control at Dryden would have little benefit at Clay Lake where only 27 percent of the mercury was derived from sediment erosion. Perturbations in mercury caused by elevated flows from the river disappear at the outflow of Clay Lake (Figure 4.6).

4.4 METHYLMERCURY

(a) Study Methods

1. Sampling Schedule

(i) 1978-79

Monthly sampling of water at all sites except 3 and 9 followed procedures outlined for total mercury. At site 9, methylmercury samples were not collected at 3 m increments. Initially, composite samples were obtained from the epi, meta and hypolimnion in Clay Lake. In the fall of 1978, the sampling program was modified to obtain samples 1 metre below the surface, 1 metre above lake bottom, plus a weighted composite sample from the water column. These changes were made to yield better information to calculate a mass balance for mercury in Clay Lake. Spot samples were obtained from the effluent at Great Lakes Forest Products Limited and from the Dryden sewage treatment plant. Samples were collected in duplicate 90 percent of the time. Weekly samples were collected at sites 7 and 10 during the ice-free season, and with even a greater frequency at site 7 during spring runoff.

(ii) 1979-80

Sampling for sites 1-10 was conducted in the same way as in 1978-79. Sites 11-17 were sampled at a depth of 1 metre. After the first 4 months of the second year of study, sampling was conducted monthly only at sites in the vicinity of Ball Lake.

2. Centrifuge Study and Loading Calculations

The procedures for these operations were the same as those described for total mercury (pp. 8-10).

3. Analytical Methods

Methylmercury is dissolved in sulphuric acid, then continuously extracted by an upward flow of condensed benzene in a liquid-liquid extractor for at least 6 hours (preferably overnight). The benzene layer is separated, extracted with aqueous thiosulphate, and potassium iodide is added. The resulting methylmercury iodide is re-extracted into benzene and analyzed by gas chromatography using an electron capture detector. The detection limit is 0.2 ng/ℓ in an 8-litre sample (Furutani and Rudd, 1980).

(b) Results and Discussion

1. Data Integrity

Duplicate samples were collected only for the first study year. The average standard deviations for duplicate samples for both years are presented in Table 4.13. Since there was good precision for duplicate samples in 1978-79, we usually collected only single samples in 1979-80. Results below detection limits were assigned values of 0.1 ng/ℓ.

2. Geographical Trends

Results of a 4-month sampling survey are found in Table 4.14. Annual and monthly methylmercury concentrations for the period July, 1979, to June, 1980, are summarized in Tables 4.15 and 4.16. A summary of results from intensive sampling of the Wabigoon River in the summer/fall of 1980 can be found in Section 4.5.

The survey during the second study year revealed that all sites could be divided into two groups. One group had methylmercury concentrations near the analytical detection limit (sites 1-6, 12-13), and the other had levels between 1.0 and 1.5 ng/ℓ (sites 7-11). Concentrations of methylmercury at control sites (sites 1, 2, and 12) were similar to other published values for uncontaminated shield systems (Chau and Saitch, 1973; Jernelov, 1975; McLean, et al., 1980).

Methylmercury levels in industrial effluent at Dryden were low (Table 4.17). Although detectable levels were recorded in effluents from the Dryden sewage treatment plant (Table 4.18), this source was also not important. The occurrence of low methylmercury concentrations at the inflow to the Wainwright Dam confirmed the negligible effect of industrial and municipal loadings. It also revealed that net methylation in this part of the river proceeded very slowly, despite the highly contaminated sediments upstream of the dam. Concentrations of methylmercury at the outflow of the dam and at the first downstream site (Minnitaki) were similar to those at the dam inflow.

At the inflow to Clay Lake, methylmercury (1.5 ng/ℓ) was nearly four times the average at Minnitaki (0.4 ng/ℓ). This difference shows that substantial methylation had occurred between these sites. Methylmercury levels dropped slightly in Clay Lake (sites 8 and 9) and at its outflow (site 10). Concentrations at the discharge of the Wabigoon River to Ball Lake averaged 1.0 ng/ℓ, and were much below this value at sites downstream of Ball Lake. The effect of methyl mercury from the Wabigoon River on the English River could not be determined since methylmercury in this area was usually below detection limit.

3. Temporal Trends

(i) Seasonal Variation

Temporal trends of methylmercury are presented in Figure 4.39. Over half the samples from Wabigoon Lake contained methylmercury below the detection limit. Concentrations slightly above this limit often occurred during warm months such as in August and September, 1978, and May and June, 1980. At Eagle River, methylmercury was also often below detection limit. A special survey (Figure 4.40) showed, however, that summer and fall values at Eagle River were an order of magnitude greater than those for winter and spring. The higher levels in 1980 are thought to be related to drought conditions.

Methylmercury concentrations at the inflow and outflow of Wainwright Dam were similar to each other but did not show any annual trends. At the inflow to Clay Lake, highest values were recorded in the summer and fall and lowest values in April. Concentrations varied annually by an order of magnitude with peak annual values of 3-4 ng/ℓ. The highest concentrations at this site were in the last samples collected, in June, 1980, when a value of 18 ng/ℓ was recorded. In the eastern basin of Clay Lake, temporal trends were similar to those at the inflow. The highest concentration at this site, 6.3 ng/ℓ, occurred in June, 1980, under drought conditions. In the western basin of Clay Lake, mercury levels also were higher in the summer and fall than in the winter and spring. Concentrations peak later in the fall than those in the eastern basin, probably because of internal cycling of methylmercury from the hypolimnion. A similar case was noted for total mercury.

Methylmercury concentrations 1 metre above the bottom of Clay Lake were often much higher than values at the surface (compare Figures 4.39 and 4.41). Mercury was inversely correlated to dissolved oxygen (Figure 4.20), with highest mercury levels in the late summer when dissolved oxygen was zero. Our initial discovery in August, 1978, of elevated methylmercury in anoxic hypolimnetic waters of Clay Lake was further explored by Furutani and Rudd (1980). By combining their data with ours, we were able to explain cycling of methylmercury in Clay Lake. After lake turnover, methylmercury levels are relatively uniform. Concentrations in mid-May, 1979, were 0.75±0.07 ng/ℓ at a depth of 1 m and 0.65±0.07 ng/ℓ at 19 m. In late October, the concentration at 1 m was 2.1 ng/ℓ and at 19 m was 1.8 ng/ℓ. During the summer, concentrations increased in the hypolimnion (Figure 4.42). After fall turnover, concentrations again rose during the winter, but to a lesser degree. In both years, the winter peak was 32 percent of the value during the preceding fall peak. Furutani and Rudd concluded that "increased methyl mercury concentrations probably resulted from diffusion away from sediment floc".

The temporal pattern of methylmercury differs from that for total mercury. We suggested that the trend for total mercury was probably due to mercury raining out as particulate matter. Evidence suggesting that algae do not carry large amounts of methylmercury into the hypolimnion is provided by data from the centrifuge study (Jackson, et al., 1983). At the outflow of Clay Lake, the similarity in concentration of methylmercury in the centrifuge effluent (0.7 ng/ℓ) and the total mercury in the influent (0.8 ng/ℓ), suggests that almost all methylmercury is in the "soluble" state. The pattern of methylmercury concentrations in hypolimnetic waters is very similar to trends of other elements that are affected by the presence or absence of oxygen. Our results suggest that anoxic conditions favour increased levels of methylmercury in Clay Lake. However, Furutani and Rudd (1980) found that anoxic sediments in the western basin and oxic sediments in eastern basin were similar in capability to produce methylmercury. Their studies on sediments from lakes in the Experimental Lakes Area in northwestern Ontario indicated that methylation of mercury occurred 2-10 times faster under anoxic conditions (J. W. M. Rudd, Freshwater Institute, Environment Canada, Winnipeg, personal communication). Regardless of how methylmercury is formed at depth in Clay Lake, elevated methylmercury in the hypolimnion affects surface concentrations at periods of lake turnover. At the outlet of Clay Lake, lake turnover doubled methylmercury levels in the fall. Methylmercury levels at this site were also high in summer and fall, and lower in the winter and spring. Weekly fluctuations in methylmercury levels at site 10 were more moderate than those at the inflow to Clay Lake.

(ii) Inter-Year Comparisons

At the Wainwright Dam inflow and outflow, mean methylmercury concentrations for 1979-80 were 33 percent and 40 percent, respectively, of their 1978-79 levels (Table 4.19). Other sites did not show this difference. The unusually high methylmercury levels in June, 1980, at sites 7 and 8 affected mean annual methylmercury levels for these sites. For example, Table 4.20, shows that excluding data for June, 1980. results in higher methylmercury averages at the outflow than the inflow to Clay Lake. Whole-lake methylmercury concentrations at Clay Lake were similar for the two years of the study (Figure 4.43), despite substantial differences in residence time.

Data for the latter half of 1980 have been included for plotting multi-year comparisons for Clay Lake inflow (Figure 4.44), eastern basin (Figure 4.45), western basin epilimnion (Figure 4.46), and outlet (Figure 4.47). In the western basin and lake outlet, concentrations of methylmercury in 1978, 1979 and 1980 were very similar. At the inflow and eastern basin, methylmercury levels in the summer of 1980 were substantially higher than levels in 1978 and 1979.

Relationships between methylmercury, temperature and flow are presented in Table 4.21. Significant relationships between temperature and methylmercury occurred at most contaminated sites. At the first contaminated site downsteam of Dryden, the inflow to Wainwright Dam, the relationship is weakly positive (Table 4.21, Figure 4.48(a)) and increases in strength at the outflow of the Wainwright Dam (Figure 4.48(b)). During high flows, concentrations of methylmercury at Wainwright Dam were relatively low and similar to those during normal flows, if temperature remained constant. Therefore, to maintain uniform concentrations, large amounts of methylmercury must have entered the water during high flows through re-suspension of sediment (Jackson et al., 1983).

At the inflow to Clay Lake, there was a strong, positive relationship between methylmercury and temperature (Figure 4.48 (c)) under a wide range of flow and temperature conditions (Figure 4.49). The second peak flow occurred at different water temperatures for different years because of watershed flow regulation. For example, during this peak, water temperatures were approximately 5°C in May, 1979, and 13°C in June, 1978. Apparently, methylmercury levels at this site were independent of flow during the spring runoff. During the study, there was a strong negative relationship between flow and methylmercury concentration (Figure 4.50), but this relationship was probably only coincidental: highest flows occurred during lowest water temperatures.

Methylmercury concentrations in Clay Lake and its outlet were also strongly temperature dependent (Figure 4.51). During the fall turnover, methylmercury concentrations increased sharply in surface waters when methylmercury in the epilimnion and hypolimnion was mixed.

4. Methylmercury Production

Methylmercury production in Wabigoon system was calculated through a mass balance of industrial and natural methylmercury loadings between Dryden and Clay Lake. Data from June to August, 1979, were compared with laboratory studies conducted under similar temperature. For June-August, 1979, the calculated flux of methylmercury at the inflow to Clay Lake was 0.53 kg. We subtracted from this value a background figure of 0.045 kg for feeder streams to yield a net monthly methylmercury production of 0.48 kg. This value was divided by the wetted area of sediment/water contact (Section 2) to obtain an average net methylmercury production rate of 1.1 μg/m^2/day for the Wabigoon River.

With fish in "Jenkins" tubes as indicators of methylmercury production in sediments, Langley (1973) and Akagi et al. (1979) determined a range of methylmercury production values for various sediments (Tables 4.22, 4.23). In comparison to values cited by these investigators, our average of 1.1 μg/m^2/day was low. However, methylmercury production is not solely related to total mercury in the sediments. Different substrates with the same total mercury level may generate very different amounts of methylmercury (Table 4.23). Much of the surface sediment in the Wabigoon River between Dryden and Clay Lake comprises silt and wood wastes (Figure 3.8), roughly similar to "silt and wood chips" in Table 4.23. Average total mercury concentrations in the surface layers of sediments in the Wabigoon River were much higher than those in Agaki's work, so we were surprised to find such low methylmercury production in the Wabigoon River. Possibly, atmospheric losses could account for some of the apparent differences in methylmercury production.

5. Steady-State Considerations

We believe that the "dynamic steady-state" proposed for total mercury also applies to methylmercury. Under steady-state conditions, methylmercury concentrations are maintained despite inflows of clean water down the system. Loading of methylmercury increases downstream. Concentrations vary with temperature at the inlet to Clay Lake.

During the summer and fall period of 1980, concentrations of methylmercury were elevated at the Wainwright Dam inflow, and generally remained similar throughout the river to Clay Lake, even though there were inputs of clean water (Section 4.5). Therefore, it appears that net production from sediments was very high above the Wainwright Dam and just downstream of the Eagle River, but much less in other areas. Methylmercury production in water is related to the time taken to reach steady-state. Our calculated methylmercury production values for the Wabigoon River were low because we incorrectly assumed that methylmercury levels were not at steady-state at the Clay Lake inflow.

Further evidence supporting the importance of the steady-state concept is provided by methylmercury levels under different residence times in Clay Lake. Methylmercury trends were very similar for the ice-free seasons in 1978, 1979 and 1980 at the western basin, and at the outlet of Clay Lake (Figures 4.46 and 4.47) despite the fact that the theoretical residence time in 1980 was five times the value for 1978 and 1979. Concentrations of methyl mercury changed little at the western basin and outlet of Clay Lake between the typical hydrological year of 1979 and the atypical 1980.

As was the case for total mercury concentrations, methylmercury values frequently fluctuated seasonally by an order of magnitude at many sites (Figure 4.39). We believe that these fluctuations fit the "dynamic steady-state" concept.

Methylmercury losses to the atmosphere may be important, particularly during low flows. Concentrations of methylmercury at many lake sites dropped simultaneously nearly an order of magnitude at the end of October, 1980 (Figures 4.44-4.47).

Factors controlling "steady-state" may include the relationship between methylmercury in water and sediments, and the relationship between methylmercury and total mercury in water. Addressing the relationship between water and sediment, only indirect evidence is available. A link can be shown between methylmercury levels in water and total mercury levels in sediments comprising organic matter overlying clay and silt (Figure 4.52). Other researchers have reported relationships between total mercury and methylmercury in sediments (Bartlet and Craig, 1981) and the existence of such a relationship in sediment would satisfactorily explain Figure 4.52 in a well-mixed system. Arguments for a methylmercury steady-state between sediment and water could also be supported by examining the source of total and methylmercury in waters at various sites. At the inflow to Clay Lake, the strong seasonal trend for total mercury appears unaffected by normal fluctuations in mill loadings; consequently, mercury in water at this site is believed to have originated in sediments. Since methylmercury here follows similar trends, concentrations may also be controlled by release from sediments.

For non-high flow conditions, the relationships between methyl and total mercury in water are plotted in Figure 4.53 and the data summarized in Table 4.24. For all eight sites, there was a highly significant relationship between total mercury and methylmercury. Atypical data for May and June, 1980, at sites 7 and 8 were excluded. Between Dryden and Clay Lake, the methylmercury fraction of total mercury increased progressively with increasing distance downstream.

At Clay Lake inflow, all available data for all non-high flow periods were plotted for three years (Figure 4.54). This figure shows that the methylmercury/total mercury relationships were very similar, despite the much higher residence time in 1980 than in the two preceding years. To examine the effects of high flow, monthly methylmercury and total mercury data for the first study year were plotted for the inflow and eastern basin of Clay Lake (Figure 4.55). The data points for the spring runoff in May, 1979 are clearly outliers. There was a strong relationship between methyl and total mercury for non-high flow periods at both sites. However, during spring runoff, the fraction of total mercury in the water increased sharply because of resuspension of river bed sediments. If total mercury concentrations in the water are in steady-state with methylmercury, the data in Figure 4.55 indicate that a large portion of the total mercury in the water during spring runoff is not immediately available for methylation. This hypothesis is supported by the centrifuge study, which showed that more than 98 percent of the mercury associated with suspended particulate matter during the spring runoff was strongly bound and potentially unavailable for methylation. It is also possible that steady-state was not achieved under these conditions.

Multilinear regressions of methylmercury on total mercury and temperature (Table 4.25) show that, in the presence of a methylmercury/total mercury steady-state, temperature is not an important factor governing methylmercury levels at most sites. For the largest data base at the inflow to Clay Lake, multilinear regressions for various flow conditions (Table 4.26) revealed that the relationship between methylmercury and total mercury could explain most of the methylmercury variance.

The relationship between mean annual methylmercury and total mercury concentrations, for sites not immediately impacted by current discharges, is shown in Figure 4.56. The data indicate site-specific differences in this relationship. For example, the ratio of methylmercury to total mercury is significantly higher for the outflow of Clay Lake than for the inflow. Factors affecting this relationship are discussed in Section 4.4.6.7.

Results from intensive sampling at 10 sites in May and June, 1980, are summarized in Tables 4.27 and 4.28. Methylmercury data are incomplete due to limitations on analytical workload. Figure 4.58 shows the data in graphical form. There is a clear relationship between methylmercury and total mercury in many portions of the Wabigoon system, under wide variations in flow and other factors. All the data were collected after peak flows, when there would be little resuspended particulate matter in the water column. Total mercury concentrations increased from Dryden to site 6(a), just upstream of the junction of the Eagle River, then declined sharply below the junction, possibly due to dilution.

Methylmercury concentrations also increased from Dryden to site 6(a), but, unlike total mercury, methylmercury concentrations were not affected by the entry of the Eagle River. The fact that substantial quantities of total mercury, but not methylmercury, were discharged from the Dryden mill complex can explain much of this pattern. For example, the source of total mercury in water at site 4, the inflow to Wainwright Dam during non-high flows only, is probably partly from the mill complex and partly from sediments. In the absence of direct anthropogenic loadings, the total mercury concentrations may well have paralleled the methylmercury concentrations. The ratio of methylmercury to total mercury at various sites (Figure 4.59) indicates that partitioning between total mercury and methylmercury in water appears complete by site 6(a), above the junction with the Eagle River. At this point, methylmercury reaches a steady-state at 5 to 7 percent of total mercury.

The centrifuge study supports the concept of a methyl/total mercury steady-state by revealing a strong relationship between total and methylmercury and between dissolved total mercury and dissolved methylmercury (Figure 4.60) for widely different aquatic environments. Kudo, et al. (1982) also found that methylmercury occurred as a constant proportion of total mercury in river waters in Canada and Japan.

6. Effects of Anoxia on Methylmercury Levels in the Wabigoon River

Very low flows in the spring of 1980 impaired the ability of the Wabigoon River to assimilate industrial organic loadings at Dryden. Anaerobic conditions developed in the upper Wabigoon and progressed downstream in a few weeks until nearly the whole river was devoid of dissolved oxygen (Section 2, Table 2.3). During and after this period, nine sites were routinely sampled. Most sampling took place between the Eagle River confluence (site 6a) and the inlet to Clay Lake (site 7), because this portion of the river remained oxic year-round.

Geographic profiles of methylmercury and dissolved oxygen for four different sampling runs are presented in Figure 4.61. During May, methylmercury levels between the Eagle River junction and the inlet to Clay Lake were similar. Although dissolved oxygen levels did not appear to affect methylmercury levels at site 6a in May, methylmercury declined here during anoxic periods in early June. At the first two sites downstream of the Eagle River, low oxygen levels were associated with a decline of about 65 percent in methylmercury. Data for selected sites (6a, b, c, d and 7) are presented in Figure 4.62. At three of the five sites (6a, d and 7), the lowering of methylmercury levels as a result of anoxia was limited to approximately one week or less. At site 7, the inflow to Clay Lake, there appears to be little oxygen effect and methylmercury appears to be mainly affected by temperature. At sites 6b and c, methylmercury levels were low during June, but by August, methylmercury was comparable to levels at the other anoxic sites (6a and d). These data suggest that the presence or absence of oxygen may affect the rate of methylation. Also, the oxygen affects the concentration of mercury once the system reaches steady-state. For example, at Minnitaki (site 6), methylmercury levels in 1979 (oxic conditions) were much lower than those in 1980 (anoxic conditions). The higher mercury levels under anoxic conditions may be due to the binding of mercury to reduced sulphur compounds which are also present in greater quantity under anoxic conditions.

7. Factors Affecting Methylmercury Concentrations in Water

The dynamic steady-state description of methylmercury levels in water in the contaminated parts of the river system can be clarified by examining published literature on methylmercury production. Many of the processes affecting methylmercury levels in water can be viewed to some extent as reversible relationships as shown in Figure 4.62.

As discussed earlier, the concentrations of methylmercury in sediments is generally believed to be the result of a reversible process (Miller, 1977; Akagi, et al., 1979, Beijer and Jernelov, 1979), Bisagni, 1979). This process may be depicted as shown below.

$$(1)\quad Hg_{inorganic} \rightleftarrows MeHg$$

Although the kinetics of the methylation and demethylation processes are not well understood, Bisogni (1979) developed an equation which described the overall net production of methylmercury.

$$(2)\quad NSMR = \gamma\,(\beta\ Hg_{total})^n$$

NSMR = net specific methylation rate

γ = coefficient determined by the microbial growth rate of the system

β = ratio of free mercuric ions to total inorganic mercury

Hg_{total} = total inorganic mercury

n = pseudo-order of the reaction

Thus, it would appear that the equilibrium (equation 1) can be shifted to the right (more methylmercury) by stimulating microbial activity, increasing inorganic mercury concentrations or increasing the fraction of mercury available as Hg^{2+}. Obviously, total mercury concentration will be one important factor. Jackson and Woychuk (1980) observed a positive linear relationship between total mercury and methylmercury levels in qualitatively similar pristine sediments from the Wabigoon River. Jackson and Woychuk

(1980) failed to find significant relationships between total and methylmercury concentrations in a biogeochemically diverse set of sediment samples from the Wabigoon River system. This suggests that environmental factors that govern the microbiology and the fraction of mercury available as Hg^{2+} can also be very important.

Because methylmercury concentrations in sediments result from a reversible process, the true production of methylmercury may be governed by how quickly the methylmercury is removed from the sediments into overlying waters. The key factors controlling the methylmercury flux from sediments will probably be the concentration gradient between the soluble methylmercury in sediments and the soluble methylmercury in water. Bioturbation may also play an important role. Interestingly, both methylmercury concentrations and methylmercury production were found to be highest at the sediment/water interface (Rudd, et al., 1983; Jackson, et al., 1980).

It has been generally thought that the source of methylmercury in water was the methylation of inorganic mercury in sediments; however, Rudd et al. (1980) and Topping and Davis (1981) have demonstrated that mercury in the water column can be methylated. Our data suggest that methylmercury levels in water can be largely affected by water column processes. This is particularly true at sites that maintain similar methylmercury to total mercury relationships over a wide range of residence times. The same factors that govern the methylmercury concentration in sediments - total mercury concentration, mercury speciation and microbial activity, may also govern the methylmercury concentrations in the water column. The suggested importance of total mercury for methylmercury formation in the water column is shown in Figures 4.53 and 4.56 and in Table 4.25. A significant percentage of the variance in these relationships remains unexplained.

The "availability" of mercury for methylation in the water column will be related to the partitioning of mercury into separate geochemical compartments. Rudd, et al., (1983) observed that radiolabelled mercury partitioned in the water column into five separate compartments, including soluble and particulate fractions, within two days. The proportion of mercury in each compartment remained stable over the duration of the experiment (60 days) even though the total mercury concentration in the water decreased exponentially. In the absence of resuspended sediments, results of our studies (Figure 4.32), also suggest that the particulate/soluble ratio of mercury in water may remain largely the same throughout the year - even though total mercury concentrations fluctuate by an order of magnitude. One possible explanation is that much of the mercury released from the sediments is in the soluble form. This mercury then partitions with particulate in the water column.

Mercury in each compartment will not be equally available for methylation. From our studies and from Dr. Rudd's studies, one can conclude that only the soluble mercury or some fraction of the mercury in the water column compartment is a major source for methylation. We suspect that much of the radiolabelled mercury in Dr. Rudd's suspended sediment experiment was adsorbed onto the newly introduced suspended sediment and was unavailable for methylation and uptake by fish. In other words, the NSMR was substantially reduced by significantly decreasing β. This would ultimately result in a higher percentage of mercury in the inorganic form by shifting the equilibrium in equation (1) to the left.

In the Wabigoon/English River system, the slopes for the methylmercury/total mercury relationships were significantly higher for contaminated sites than for control stations (Figure 4.53, MOE, 1980 unpublished data). The higher slopes at the contaminated sites may simply result from a shift of the total mercury-methylmercury equilibrium (equation 1) to the right. This may be caused by an increase in the total mercury supply from diffuse sources and an increase in microbial activity stimulated indirectly by phosphorus loadings from Dryden.

One can interpret the results of the bottom-sealed-tube experiment conducted by Dr. J. W. Rudd, et al. (1980) in the same way. Higher inorganic concentrations were evident in the water column in the bottom-sealed tube. Microbial activity likely increased in response to nutrient additions. Both these factors would increase the NSMR or result in higher methylmercury concentrations at equilibrium.

The aforementioned processes contribute to a situation we have described as a "dynamic steady-state". We recognize that this is not a true steady-state, because biota data (Section 5) imply that both inorganic and methylmercury are slowly being lost from the ecosystem (through sedimentation, losses to the atmosphere and water column export). Many of the steady-state relationships which affect methylmercury levels in water, were found to be complete within hours or days. Thus, in very slow moving streams and lakes, methylmercury concentrations in the water column should be controlled principally by local environmental variables.

Evidence that methylmercury is locally generated is shown by data for the inflow and eastern basin of Clay Lake (Figure 4.64). Methylmercury trends at both sites were similar, particularly in 1979, with no suggestion of a lag in levels of the eastern basin. A lag of approximately 11 days under normal flows would be expected if methylmercury was derived from the inflow of the Wabigoon River. Methylmercury concentrations at the Clay Lake inflow and eastern basin were atypically low during the 1979 August to September period in comparison to seasonal trends for 1978 and 1980. During this period, samples were also collected from 10 m diameter enclosures in the experimental bay in the eastern basin. Waters in these enclosures was isolated from Clay Lake waters, yet results were very similar to values from nearby sites in Clay Lake (Figure 4.65). These results constitute strong evidence that methylmercury concentrations in water in Clay Lake are indeed dynamic and the result of local environmental variables.

In the Wabigoon River between Dryden and Clay Lake, where there are significant changes in the aquatic environment, it is difficult to determine which factors govern methylmercury levels. At upstream sites (i.e. Wainwright Dam) travel time, industrial discharges, and sediment type may all influence steady-state concentrations of methylmercury.

In the Wabigoon River from Dryden to Clay Lake, there is a decreasing quantity of wood chips and an increase in sand and gravel (Section 3). Akagi et al., 1979, suggest that, at steady-state, higher methylmercury might be expected over sand and gravel than over wood chips and other organic waste.

8. Transport (Loadings)

(i) Geographical Trends

Methylmercury loadings for the second year of the study are presented in Table 4.29. For most sites, annual loading values are semi-quantitative because many samples had methylmercury levels below the detection limit. There was a very large increase in the loadings from Dryden to the inflow to Clay Lake, followed by a moderate increase to the inflow to Ball Lake. Methylmercury loadings from the Wabigoon River had no apparent effect on the English River system. Because the second study year was hydrologically atypical, we calculated loadings for a normal hydrological year using steady-state principles, concentration data and long-term mean flows. Assuming that the natural methylmercury levels in water are 0.25 ng/ℓ, that the long-term English/Wabigoon River flow ratio = 6:1, and that the methylmercury level at the Wabigoon River inflow to Ball Lake, is 1.0 ng/ℓ at steady-state, then the anthropogenic methylmercury loadings at the Wabigoon River influx accounted for about 30 percent of the methylmercury flux at Ball Lake outflow.

The annual flux for the Wabigoon Lake outflow was 0.05 kg. The annual loadings at sites 4 and 5, immediately downstream of Dryden, were 0.06 and 0.07 kg respectively, which indicated that little net methylation had occurred in the waters between Dryden and the outflow of the Wainwright Dam. The loading at the outflow of the Wainwright Dam was only slightly higher than the inflow. Loadings increased at Minnitaki to 0.19 kg, and at the inflow to Clay Lake to 1.0 kg. There was proportionately much more methylmercury produced in the Wabigoon River between Minnitaki and Clay Lake than between Dryden and Minnitaki (Figure 4.66). Methylmercury partitioning may not have been complete at Minnitaki, or substrate characteristics may have favoured a lower methyl mercury sediment/water partitioning coefficient (ratio of various forms of mercury within and between ecosystem components) for the lower reaches.

After subtracting natural methylmercury loadings at the inflow to Clay Lake, approximately 85 percent of the annual flux at this point is related to anthropogenically released mercury. Because steady-state is reached before Clay Lake, loadings at the lake inflow and outflow were similar. The loading remained about the same at the inflow to Ball Lake. The anthropogenically-related methylmercury flux from the inflow to Clay Lake to the inflow to Ball Lake was 83-86% of the total methylmercury loading.

(ii) Temporal Trends

Monthly methylmercury loadings are presented in Figure 4.67. River sites show less evidence of seasonal trends than lake sites. The probable reason for this difference is the effect of flow regulation at Wabigoon Lake and the Eagle River. Controlled flows would mask any trends that might be present during natural seasonal flows.

Although there are no temporal trends for methylmercury loadings at either the inflow or outflow of Wainwright Dam, there were strong similarities in paired monthly loadings between these two sites.

At the inflow to Clay Lake, monthly loadings were highest in the summer and lowest in the winter. Figure 4.68 reveals that daily loadings in June are similar to those in the spring runoff because of the increase in methylmercury concentration with water temperature. The difference in loadings for the two spring runoff peaks is probably due to exhaustion of sediment flushed from the river bed during the first peak. The total methylmercury load for the complete spring runoff was only 17 percent of the annual flux.

Methylmercury loadings at the outflow of Clay Lake followed the same seasonal trends found at the inflow.

4.5 MERCURY IN THE WABIGOON RIVER UNDER LOW FLOW CONDITIONS IN 1980

At the end of the federal/provincial study in June, 1980, the Ontario Ministry of the Environment conducted an additional survey of mercury under conditions of very low flow in the Wabigoon River. Data from this study were intended to assist in decisions relating to pollution control programs at Great Lakes Forest Products Limited, Dryden.

Water samples were collected weekly for 10 weeks, beginning August 4, 1980, at 13 sites (Figure 4.57). Most of the river was anoxic during much of the study period. At the junction of the Eagle River, where there is a large influx of uncontaminated water, sampling was more intensive than at other sites. To ensure that flows from the Eagle and Wabigoon were completely mixed at site 6B, cross-sectional investigations were conducted with a YSI conductivity meter. Mercury analysis of samples were performed at the Freshwater Institute, Environment Canada, Winnipeg. Physical and chemical properties of samples were also defined, using methods outlined in Section 2.

Mean total mercury levels (Figure 4.68) were about the same at all sites, including the eastern basin of Clay Lake, during the survey period. Flow rates and time-of-travel

(Figure 4.69) show that mercury levels were not affected by the duration of contact between sediment and water. Likewise, the large inflows of clean water from the Eagle River had no effect on mercury levels downstream. This stability suggests that mercury had partitioned between water and sediment throughout the system and had achieved a steady-state. As partitioning was complete at the first site downsteam of Dryden, steady-state was reached in a day or less. Much of the variability in total mercury is related to seasonal effects. Seasonal differences are shown in Figure 4.70. From August to October, mercury followed the same trends at different sites, then dropped sharply about an order of magnitude in mid-October (Figure 4.71). The figure also shows that mercury concentrations dropped at the outflow of Clay Lake before declining at upstream sites, suggesting that the effects of upstream loadings were not important below Clay Lake. Large amounts of mercury may have been lost to atmosphere. The effects of residence time at any site can also be examined by plotting mercury concentrations, flow and temperature. Data for site 7, the inflow to Clay Lake, is shown in Figure 4.72. The residence time of the river increased substantially in the summer of 1980. Mercury concentrations at this time were generally about 1.5 times the concentrations for comparable seasons in previous years. Increases in concentrations in 1980 may be attributed to residence time effects and/or to concomittant changes in water chemistry (Ontario Ministry of the Environment, unpublished data). Mercury concentrations at all lake sites during the ice-free season in 1980 were also about 1.5 times the concentrations observed in previous years (Figures 4.24-4.26). In 1980, the theoretical residence time for Clay Lake in May and June increased by 3 and 10 times respectively above the long-term mean. Between July and November, 1980, the estimated residence time increased by a factor of at least five over the mean. In 1978 and 1979 the hydrology was near the long-term mean (Section 2).

With the exception of sites at the inflow to the Wainwright Dam and in Clay Lake, average methylmercury levels also fell within a narrow range, and were rarely dependent on time of contact between water and sediment (Figure 4.73). If time of contact was important, methylmercury would progressively increase downstream of Dryden. Like total mercury, methylmercury levels were not influenced by inflows of the Eagle River. These findings support our conclusion that mercury partitioning was complete throughout the system and had reached steady-state a short distance downstream of Dryden. Since industrial releases of methylmercury at Dryden were minimal, we believe that processes within the river determined methylmercury levels at all sites. Between sites 5 and 5A, mercury was either demethylated or lost to atmosphere. The two peaks of methylmercury in August and September (Figure 4.74) were similar to trends noted in Clay Lake in 1979 (Figure 4.42) and at Eagle River in 1979 and 1980 (Figure 4.43). In contrast to earlier surveys, methylmercury levels at the Wainwright Dam outflow were sharply higher than those at the inflow. The lowering of the reservoir to repair the dam may have caused this situation. Methylmercury at control sites in Wabigoon Lake and Eagle River were also three and six times, respectively, values recorded in earlier years. This effect may have been related to the drought conditions prevailing during late 1980.

4.6 SITE-SPECIFIC RELATIONSHIPS BETWEEN TOTAL MERCURY, METHYLMERCURY AND OTHER PARAMETERS FOR NON-HIGH FLOW PERIODS

Because the sample size for some parameters was too small to conduct factor analysis, we constructed diagrams known as "correlellograms" (McQuinty, 1957). Correlellograms demonstrate the more important interactions between mercury and other environmental variables. Figure 4.75 presents correlellograms for 10 sites on the Wabigoon River system. A positive sign indicates a positive relationship between two variables. The number of lines joining two variables is related to the significance of the relationship: one line for 95 percent probability, two for 99 percent, and three for 99.9 percent. Table 4.30 lists the correlation coefficients between mercury and other water quality parameters. Likewise, Table 4.31 lists correlation coefficients between methylmercury and other water quality parameters. The correlellograms progressively increased in complexity with increasing distance downstream. At Clay Lake, this trend was reversed. The diagrams suggest a very dynamic system, with large differences in total mercury and methylmercury cycling at each site even though both are nearly always strongly correlated. Industrial loadings at Dryden probably have had a greater impact on total mercury levels than on methylmercury. At the inflow to Clay Lake, however, both total mercury and methylmercury levels in the water may result from mercury released from sediment. The significance of sediment as a mercury source is shown by the statistical strength of common relationships. A comparison of inflow and outflow correlellograms for Clay Lake suggests that the lake may trap total mercury, but not methylmercury.

Correlation coefficients between total mercury concentrations, temperature, pH, and conductivity are illustrated in Figure 4.76. The correlation between pH and mercury was weak and positive at Wabigoon Lake, but negative at the next three monitoring sites downstream. A negative correlation is expected in a metal-enriched system: at lower pH values, more mercury could be leached from contaminated sediments. In Clay Lake, however, the relationship was positive and statistically significant at sites 8 and 9. This unusual situation can be explained by examining the relationships between temperature and pH. This relationship was strongly positive at lake sites, presumably due to effects of photosynthesis. The best example is site 10 (Figure 4.77), where, a regression of pH of temperature yielded a correlation coefficient of 0.77 at $p<0.001$ (Section 2, Appendix 2-B). Evidently, temperature effects were much stronger than pH effects at lake sites.

Trends for conductivity were the inverse of those for pH. Conductivity and mercury are positively correlated at most river sites. Salts in industrial effluent at Dryden presumably increased conductivity and mobilized mercury from sediment. At lakes sites, however, the correlation between total mercury and conductivity was negative.

At Wainwright Dam, mercury concentrations are affected by industrial discharges at Dryden. Downstream, however, mercury levels are governed more by mercury released from sediments. At the inflow to Clay Lake, seasonal factors (mainly temperature) determine mercury concentrations, as shown by the correlellograms for this location. In the eastern basin of Clay Lake, temperature is also the key factor affecting mercury levels but primary productivity also plays a role. The positive correlation between pH and total mercury in Clay Lake is likely a secondary relationship derived from the probable connection between productivity and pH. For the same reason, conductivity is also considered of secondary importance. The relationship of total mercury and suspended solids is separate from other interactions.

Mercury in the western basin undergoes internal cycling. Some of the mercury deposited on the bottom with dying algae during the summer re-appears on the surface during fall turnover, when temperatures are approximately 4-6°C. This process eliminates the possibility of developing an annual relationship between temperature and mercury in this part of the lake. Internal cycling of mercury also strongly affected mercury levels at the outflow of the lake.

Correlations between methylmercury and pH, conductivity, and temperature are presented in Figure 4.78. Temperature strongly influenced methylmercury at most sites. There was little relationship between pH and methylmercury levels at Wainwright Dam, but positive relationships occurred in the eastern and western basins of Clay Lake. We believe that the pH-methylmercury relationship in Clay Lake results from two separate phenomena that are both related to temperature. The correlation with conductivity was positive at downstream river sites and negative in Clay Lake, with a statistically significant relationship at the outflow, but not at the inflow. The correlellograms also reveal that the Wainwright Dam has a strong effect on the binding of methylmercury, despite a residence time of only a few hours. At the outflow of Wainwright Dam, there is a very strong relationship between methylmercury and sulphate, and between sulphate, sodium, suspended solids, and conductivity. We believe that the methylmercury-sulphate relationship is primary, while methylmercury-sodium, conductivity and suspended solids relationships are both secondary and weaker. Manganese and chloride were implicated in the chemistry of methylmercury at this site and appeared to be part of a separate factor. All chemical parameters were unrelated to temperature or flow at Wainwright Dam. While the Dryden mill discharges little methylmercury, effluents from the source, combined with sediment at Wainwright Dam, have a strong influence on the chemistry of methylmercury downstream. Mechanisms relating methylmercury and sulphate levels are unknown. Sulphate levels are controlled primarily by mill discharges. With elevated sulphate, there may be a selective affinity between an anion and cation that accounts for the relationship between methylmercury and sulphate. Sulphate may "leach" methylmercury from sediments containing high methylmercury levels (Jackson and Woychuk, 1980).

The relationship between methylmercury and conductivity was negative at the eastern basin of Clay Lake and remained negative at the other lake sites. The inverse relationship between temperature and conductivity probably governs the conductivity/methylmercury relationship.

At both control sites, there was a strong link between methylmercury and suspended solids. The Eagle River sampling point is considered similar to a lake site in that it is immediately downstream from the lake outflow. Suspended solids concentrations at both control sites are probably related to organic particulate matter. The presence of organic matter may also account for positive relationships between methylmercury and iron and manganese, and may stimulate methylmercury production (Rudd, et al., 1980). This phenomenon could also explain the methylmercury-total phosphorus relationship in the eastern basin of Clay Lake because of the well-established relationships between total phosphorus and phytoplankton (Schindler, et al., 1978). These biological effects could also explain the relationships between methylmercury and iron at sites 2, 7 and 11, and manganese at sites 2 and 7.

4.7 CONCLUSIONS

(a) TOTAL MERCURY

1. Ten years after major mercury loadings from an industrial source were sharply reduced, mercury levels in the waters of the Wabigoon River system downstream of Dryden remained markedly elevated. The mercury concentration immediately downstream of Dryden averaged nearly five times the mean value at the control site and was still three times the control at the inflow to Ball Lake, 150 km downstream of Dryden. Below this point, mercury levels were lower and were frequently below detection limit.
2. Elevated mercury levels in the Wabigoon River can be attributed to effects of current mill discharges, chemical and biological remobilization of mercury from sediments, and erosion of mercury-enriched sediments during high flows.
3. Current industrial discharges affect only the upper portion of the Wabigoon River. During regulated flood flows, mercury concentrations in this part of the river were elevated by more than an order of magnitude because of the resuspension of contaminated sediments. The most pronounced effects were noticed at sites immediately downstream of Dryden. At the inflow to Clay Lake, the effects of regulated flood flows were similar to those during unregulated runoff. Flood

conditions had much less effect on mercury concentrations at this location than at upstream sites. Mercury levels at the inflow to Clay Lake and in Clay Lake itself were affected by temperature. Mercury levels at the lake outflow were modified by internal lake cycling of mercury and may be influenced by biological productivity.

4. Mercury losses to the atmosphere may be significant, particularly during low flow periods.

5. In the absence of resuspended sediment during high flows, mercury levels in contaminated waters can be best described as being in a "dynamic steady-state". This condition is established within a few days. Under steady-state conditions, mercury concentrations are independent of travel time and loadings, and largely independent of residence time. The steady-state condition is termed dynamic because mercury concentrations at many sites fluctuate seasonally by an order of magnitude. Temperature appears to be an important controlling variable. Changes in the residence time and biogeochemical characteristics are of secondary importance.

6. During the study, mercury loadings from Great Lakes Forest Products Limited were about 10 kg per year, or about five times the background loading from Wabigoon Lake.

7. The present effect of the Wainwright Dam on total mercury concentrations and loadings in the upper Wabigoon River is negligible. However, the large quantity of mercury currently contained behind the dam may be cause for concern in the future.

8. Clay Lake acts as a significant sink for total mercury entering via the Wabigoon River. About one-third of total incoming mercury is retained in the lake during a typical hydrological year. During qn atypical low flow year (1980), 45 percent was retained by Clay Lake.

9. Resuspended sediments from the river bed contribute up to 50 percent of the total annual loading of mercury in the upper Wabigoon River during controlled floods. The total mercury flux in the upper Wabigoon River can be controlled by the rate of release of water at Dryden. The maximum daily flux in the river at Minnitaki was equivalent to approximately 12 percent of the annual loading to Clay Lake.

10. Because some eroded sediment settles out in the middle reaches of the river, mercury concentrations entering Clay Lake during high flows were about the same whether the flows were predominantly from regulated discharge at Dryden or from unregulated runoff. In 1979 (a typical hydrological year), about 25 percent of the mercury entering Clay Lake was associated with resuspended bed sediment transported during high flows.

11. Industrially-related mercury accounts for about 70-80 percent of the annual flux at the mouth of the Wabigoon River, but only for about 20 percent at the outflow from Ball Lake.

12. Mercury levels in the water column are influenced by both local and upstream sources of mercury. The influence of upstream sources results from: (a) the release of mercury from bottom sediments during the time required to achieve steady-state and the downstream transport of this mercury in the water column, and (b) the resuspension and transport of bottom sediment by high flows.

(b) METHYLMERCURY

1. Aquatic concentrations of methylmercury at most sites downstream of Dryden were elevated in comparison to control sites. However, the impact of methylmercury discharged by the Wabigoon River into the English River system could not be assessed because methylmercury in many samples from the English River were below the detection limit.

2. Methylmercury from the industrial source and municipal sewage treatment plant at Dryden had negligible effect on methylmercury levels in the receiving stream.

3. Elevated methylmercury concentrations in waters were caused by methylation of inorganic mercury in sediments and water, effects of current mill discharges on leaching of methylmercury from sediments, and the erosion of methylmercury-enriched sediments during floods.

4. The immediate effects of current industrial effluents were limited to the upper portion of the Wabigoon River under normal hydrological conditions. Increased methylmercury concentrations at river sites during spring runoff were mainly due to the resuspension of methylmercury-enriched sediments. Methylmercury concentrations at the inflow to Clay Lake and in Clay Lake were strongly correllated with total mercury concentrations and temperature, and were very dynamic. The effects of high flows were negligible. Methylmercury concentrations at the outflow of Clay Lake are modified by internal lake cycling.

5. During non-high flows, when significant quantities of resuspended sediment were absent, methylmercury levels were in a steady-state between sediment and water or in a steady-state between methylmercury and total mercury in the water column. Once steady-state was achieved, methylmercury levels in waters were independent of time of travel or time of contact with sediments. Mercury on resuspended contaminated sediment is not immediately available for methylation.

6. Methylmercury concentrations in waters in this heavily contaminated ecosystem depend upon the rate of release from sediments to water, the rate of release from water to air, and the biogeochemical characteristics of the water column.

7. Methylmercury and other mercury compounds in water and sediment form reversible reactions, resulting in a dynamic system. Methylmercury concentrations in water achieve steady-state conditions rapidly - within hours or a few days.

8. Mercury methylation may occur more slowly under anoxic conditions, but once steady-state is reached, methylmercury levels in the river are higher under anoxic conditions.

9. Methylmercury levels at each site appear similar from year-to-year. This phenomenon suggests that the river system will continue to function in the manner described unless there are major changes in the system.

10. The present effect of the Wainwright Dam on methylmercury production is negligible under all but very low flow conditions.

11. Clay Lake is not a sink for methylmercury entering via the Wabigoon River.

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TABLE 4.1. Mean, depth-integrated mercury concentrations in samples from the Wabigoon River, site 4, August 23, 1978.

Cross Section[a] Depth (m)	Total Mercury (ng/ℓ)	Filtrate Mercury (ng/ℓ)	Percent Mercury[b] on Particulate Matter
0.7	40	14	65
1.8	38	22	42
2.4	24	20	16
3.0	28	16	42
3.0	58	18	69
1.4	44	13	70
1.9	40	14	65
1.1	86	46	46
0.5	26	23	12
0.6	30		
Average	41	21	47

[a] In 10 percent increments across the river from left to right facing upstream.

[b] By difference between columns 3 and 2.

TABLE 4.2. Vertical profile of mercury concentrations in samples from the Wabigoon River, site 4, August 23, 1978.

Midstream Depth (m)	Mercury Concentration (ng/ℓ)
0.3	20
	23
1.0	21
	20
1.6	31
	17
2.3	25
	17
3.0	17
	28

TABLE 4.3. Variability in total mercury concentrations associated with sampling and analytical methods.

Site[a]	Number of samples	% of analyses above detection limit	Average standard deviation of means of duplicate samples (ng/ℓ)
1 Wabigoon Lake	116	45	3.5
3 G.L.F.P. Ltd.	173	99	
4 Wabigoon River inflow to Wainwright Dam	145	99	7.2[b]
5 Wabigoon River outflow of Wainwright Dam	137	95	5.1[b]
6 Wabigoon River at Minnitaki	94	98	3.8[b]
2 Eagle River	82	29	1.8
7 Wabigoon River inflow to Clay Lake	103	97	4.1
8 Clay Lake, eastern basin	105	98	2.9
9 Clay Lake, western basin, epilimnion	99	96	3.0
10 Wabigoon River outflow to Clay Lake	101	97	3.1
11 Wabigoon River inflow to Ball Lake	21	100	
12 English River inflow to Ball Lake	20	35	
13 English River outflow to Ball Lake	20	40	
14 Lount Lake	8	38	
15 Umfreville Lake	8	0	
16 Sand Lake	8	25	
17 Eaglenest Lake	8	38	

[a] See Figure 4.3.

[b] During non-high flow period.

TABLE 4.4. Mean total mercury concentrations in the Wabigoon/ English River system, July, 1979 - June, 1980.

Site[a]	N[b]	Concentration (ng/ℓ)	
		Mean	Monthly Range
1 Wabigoon Lake	44	5	<5-14
3 Great Lakes Forest Products	42	194	
4 Wabigoon River, inflow to Wainwright Dam	46	24	12-30
5 Wabigoon River, outflow of Wainwright Dam	46	25	8.5-34
6 Wabigoon River at Minnitaki	46	23	12-35
2 Eagle River	47	3	<5-9
7 Wabigoon River, inflow to Clay Lake	45	29	17-46
8 Clay Lake, Eastern Basin	46	25	10-46
9 Clay Lake, Western Basin	44	16	7.5-22
10 Wabigoon River, outflow of Clay Lake	43	19	12-26
11 Wabigoon River, inlet to Ball Lake	21	14	9-27
12 English River, inflow to Ball Lake	20	5	<5-10
13 English River, outflow of Ball Lake	20	8	<5-21

[a] See Figure 4.3.

[b] Number of samples.

TABLE 4.5. Mean monthly total mercury concentrations (ng/ℓ) for surface waters in the Wabigoon/English River system, July, 1979-June, 1980.

Site[a]	N[b]	1979						1980					
		Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	June
1 Wabigoon Lake	44	4	7	5	5	4	<5	<5	<5	<5	5.5	8.5	14
4 Wabigoon River, inflow to Wainwright Dam	46	22	21	22	25	19	12	20	25	30	32	34	30
5 Wabigoon River, outflow of Wainwright Dam	46	18	26	25	34	22	8.5	11	25	34	32	26	34
6 Wabigoon River at Mannitaki	46	22	31	28	27	20	13	16	14	12	28	26	35
2 Eagle River	47	3	3	<5	3.5	4	<5	<5	<5	<5	4	<5	9
7 Wabigoon River, inflow to Clay Lake	45	39	29	22	33	31	29	17	17	17	23	32	54
8 Clay Lake, eastern basin	46	29	29	39	46	28	9.5	18	14	10	11	26	38
9 Clay Lake, western basin epilimnion	44	12	16	18	22	20	17	10	9	7.5	13	25	19
10 Wabigoon River, outflow of Clay Lake	43	12	18	20	21	19	16	16	17	18	22	26	20
11 Wabigoon River, inflow to Ball Lake	21	7.5	9.5	10	12	16	20	27	18	8	11	13	16
12 English River, inflow to Ball Lake	20	<5	9	<5	<5	<5	<5	10	9.5	9	7	6	<5
13 English River, cutflow of Ball Lake	20	<5	<5	<5	<5	12	21	16	14	11	8	5	4

[a] See Figure 4.3.

[b] Number of samples.

N.B.: November, February and April data are interpolated.

TABLE 4.6. Total mercury concentrations (ng/ℓ) for surface waters in the Wabigoon-English-Winnipeg River system, July to October, 1979.

Site[a]		Date Jul 10/11	 Aug 7/9	 Sep 4/5	 Oct 2/3	Mean
1	Wabigoon Lake	4	6	5	3	4.5
3	G.L.F.P. Ltd. effluent	130	370	250	n/a	250
4	Wabigoon River, inflow to Wainwright Dam	22	26	24	25	24
5	Wabigoon River, outflow of Wainwright Dam	18	26	25	34	26
6	Wabigoon River at Minnitaki	22	31	28	27	27
2	Eagle River	3	3	2	2	2.5
7	Wabigoon River, inflow to Clay Lake	39	29	22	33	31
8	Clay Lake, eastern basin	29	29	39	46	36
9	Clay Lake, western basin	12	16	18	19	16
10	Wabigoon River, outflow of Clay Lake	12	17	20	21	18
11	Wabigoon River, inflow to Ball Lake	8	10	10	12	10
12	English River, inflow to Ball Lake	2	9	2	2	3.8
	Ball Lake, north basin	2	8	5	-	5.0
	Ball Lake, south basin	2	2	2	12	4.5
13	English River, outflow of Ball Lake	2	2	2	2	2.0
14	Lount Lake	2	4	2	24	8.0
15	Umfreville Lake	2	2	2	2	2.0
16	Sand Lake	2	5	6	2	3.8
17	Eaglenest Lake	2	2	5	9	4.5

[a] See Figure 4.3.

TABLE 4.7. Mercury concentrations (ng/ℓ) in Wabigoon Lake and in five uncontaminated tributaries of the Wabigoon River, August 2, 1978 to August 1, 1979.

Sampling Site	1978					1979						
	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul
Wabigoon Lake	19(8)[a]	8(8)	4(8)	2(4)	13(2)	10(8)	5(2)	2(2)	4(10)	6(11)	3(8)	4(8)
Eagle River			2(2)					2(2)	6(12)	4(12)	6(8)	3(8)
Aubrey Creek			2(2)					6(2)	7(2)			
Buller Creek			2(2)						7(2)			
Hutchinson Creek			2(2)					2(2)	10(3)			
Rugby Creek			2(2)					2(2)	4(2)			

[a] Monthly average mercury concentrations, with number of samples per month shown in parentheses.

TABLE 4.8. Correlation coefficients for linear regressions between total mercury and flow and between total mercury and temperature.

Site	Temperature	Flow
Eagle River	.19/22/.33[a]	.08/38/.64
Wabigoon Lake	.10/51/.50	
Inflow to Wainwright Dam[b]	.07/50/.65	.11/50/.45
Outflow of Wainwright Dam[b]	.30/50/.04[c]	.04/50/.79
Minnitaki[b]	.23/30/.22	-.42/30/.02
Clay Lake, inflow	.73/66/.00	-.48/24/.02
Clay Lake Eastern Basin	.46/48/.00	
Clay Lake Western Basin	.19/50/.10	
Clay Lake outflow	.20/52/.08	-.20/52/.13
Inflow to Ball Lake	-.32/11/.33	

[a] Correlation coefficient/number of observations/statistical/significance.

[b] For non-high flow periods (see Section 2).

[c] Statistically significant (p<.05) relationships are underlined.

TABLE 4.9. Monthly mercury profiles, Clay Lake, Western Basin (site 9), June, 1979 to June, 1980.

	Mercury Concentration (ng/ℓ)										
Depth (m)	Jun 13	Jul 11	Aug 9	Sep 5	Oct 3	Oct 31	Dec 18	Jan 8	Mar 4	May 7	Jun 25
1	11	14	12	18	16	24	17	10	8	19	20
4	10	24	15	16	15	24	18	95	6	14	16
7	8	11	16	11	15	20	16	10	8	16	18
10	12	16	20	14	16	12	24	14	7	18	16
13	12	13	14	19	15	23	18	18	14	14	17
16	10	15	16	28	16	21	20	18	16	13	17
19	4	36	31	40	32	22	28	22	20	17	16

TABLE 4.10. Mean total mercury concentrations (ng/ℓ) for monitoring sites in the Wabigoon/English River System for two study periods.

	August,1978 - July, 1979			July, 1979 - June, 1980			Mean for two periods
	N[a]	Mean	Monthly Range	N[a]	Mean	Monthly Range	
1 Wabigoon Lake	80	9	2.5-18	44	5	2.5-14	7.0±2.83
2 Eagle River				47	3	2.5-9	
3 Great Lakes Forest Products Limited	78	294		42	194		
4 Wabigoon River inflow to Wainwright Dam	98	27	1.5-48	46	24	12-30	25.5±7.12
5 Wabigoon River outflow of Wainwright Dam	98	23	2.5-42	46	25	8.5-34	24.0±1.41
6 Wabigoon River at Minnitaki				46	23	12-35	
7 Wabigoon River inflow to Clay Lake	94	25	9.0-45	45	28	17-46	26.5±2.12
8 Clay Lake eastern basin	67	22	2.5-49	46	25	10-46	23.8±1.77
9 Clay Lake western basin - epilimnion	65	17	4.0-39	44	16	7.5-22	16.5±0.71
10 Wabigoon River outflow of Clay Lake	66	14	4.0-23	43	19	12-26	16.5±3.54
11 Wabigoon River inflow to Ball Lake				21	14	9-27	
12 English River inflow to Ball Lake				20	5	2.5-10	
13 English River outflow of Ball Lake				20	8	2.5-21	

[a] Number of samples.

TABLE 4.11. Dissolved mercury concentrations (ng/ℓ) at selected sites in the Wabigoon River system, April-September, 1979.

	April	May	July	Sept
Eagle River	<5	18	12	4.2
Wabigoon Lake	<5	6	<5	<5
Wainwright Dam Inflow	77	7	18	26
Wainwright Dam Outflow	14	5.5	17	18
Minnitaki	7.3	30	22	51
Quibell	12	14	22	32
Clay Lake Outflow			12	

TABLE 4.12. Loadings of total mercury in the Wabigoon River system, July, 1979 - June, 1980.

Site	Annual Loading (kg)	Monthly Range (kg)
1 Wabigoon Lake	1.0(0.46-1.5)[a]	0.01-.18
3 Great Lakes Forest Products Ltd.	9.7	n/a
4 Inflow to Wainwright Dam	7.4	0.26-1.1
5 Outflow of Wainwright Dam	7.4	0.29-1.2
6 At Minnitaki	9.1	0.32-2.2
2 Eagle River	1.2(0.25-2.4)[a]	0.05-1.4
7 Inflow to Clay Lake	26.6	1.1-3.7
10 Outflow from Clay Lake	18.6	0.39-3.1
11 Inflow to Ball Lake	18.9	0.49-3.1
12 English River Inflow to Ball Lake	70(30-190)[a]	1-13
13 English River Outflow from Ball Lake	130(74-144)[a]	2-30

[a] >10% of mercury results were below detection limits; therefore, upper and lower bounds on loadings are given. The upper one equates the "less than" value to 5 ng/ℓ, the lower one equates it to 0.

TABLE 4.13. Variability in methylmercury concentrations associated with sampling and analytical methods in this study.

	Number of Samples	% of Analyses above Detection Limit	Average Standard Deviation of Duplicate Sample Means
1 Wabigoon Lake	40	48	.056
3 G. L. F. P. Ltd.	12	50	
4 Wabigoon River inflow to Wainright Dam	36	67	.071
5 Wabigoon River outflow of Wainwright Dam	35	63	.065
6 Wabigoon River at Minnitaki	20	80	
2 Eagle River	31	45	.023
7 Wabigoon River inflow to Clay Lake	75	96	.199
8 Clay Lake, eastern basin	38	97	.161
9 Clay Lake, western basin, epilimnion	36	97	.229
10 Wabigoon River outflow of Clay Lake	73	97	.154
11 Wabigoon River inflow to Ball Lake	12	100	
12 English River inflow to Ball Lake	12	50	
13 English River outflow of Ball Lake	12	66	
14 Lount Lake	4	50	
15 Umfreville Lake	4	50	
16 Sand Lake	4	75	
17 Eaglenest Lake	4	75	

[a] See Figure 4.3.

TABLE 4.14. Methylmercury concentrations (ng/ℓ) for surface waters in the Wabigoon/English River system, July to October, 1979.

Site[a]	Sampling Date				
	Jul 10-11	Aug 7-9	Sep 4-5	Oct 2-3	Mean
1 Waigoon Lake	0.1	0.1	0.1	0.2	0.12
4 Wabigoon River, inflow to Wainwright Dam	0.1	0.1	0.1	0.2	0.12
5 Wabigoon River, outflow of Wainwright Dam	0.1	0.2	0.1	0.1	0.12
6 Wabigoon River at Minnitaki	0.5	0.4	0.2	0.1	0.30
2 Eagle River	0.2	0.2	0.1	0.6	0.28
7 Wabigoon River, inflow to Clay Lake	2.0	1.1	0.3	1.2	1.2
8 Clay Lake, eastern basin	1.8	1.0	0.5	1.3	1.2
9 Clay Lake, western basin	1.8	1.0	1.9	2.8	1.9
10 Wabigoon River, outflow of Clay Lake	1.5	1.4	4.6	3.4	2.7
11 Wabigoon River, inflow to Ball Lake	0.4	0.3	0.6	--	0.43
12 English River, inflow to Ball Lake	0.1	0.2	0.2	--	0.17
13 English River, outflow of Ball Lake	0.2	0.1	0.1	--	0.13
14 Lount Lake	0.2	0.1	0.1	0.8	0.30
15 Umfreville Lake	0.2	0.1	0.1	0.3	0.18
16 Sand Lake	0.2	0.1	0.2	0.4	0.22
17 Eaglenest Lake	0.3	0.1	0.3	0.6	0.32

[a] See Figure 4.3.

TABLE 4.15. Mean methylmercury concentrations for monitoring sites in the Wabigoon/English River system, July, 1979-June, 1980.

Site[a]	N	Concentration (ng/ℓ)	
		Mean	Monthly Range
1 Wabigoon Lake	16	≅.32	0.1 - 0.5
4 Wabigoon River inflow to Wainwright Dam	13	≅.24	0.1 - 0.9
5 Wabigoon River outflow of Wainwright Dam	13	≅.26	0.1 - 1.1
6 Wabigoon River at Minnitaki	14	≅.44	0.1 - 1.7
2 Eagle River	23	≅.18	0.1 - 0.6
7 Wabigoon River inflow to Clay Lake	27	1.5	0.3 - 7.4
8 Clay Lake, eastern basin	12	1.2	0.2 - 4.1
9 Clay Lake, western basin	11	1.2	0.3 - 2.1
10 Wabigoon River, outflow of Clay Lake	24	1.3	0.4 - 1.9
11 Wabigoon River, inflow to Ball Lake	12	1.0	0.4 - 2.1
12 English River, inflow to Ball Lake	12	≅.25	0.1 - 0.5
13 English River, outflow of Ball Lake	12	≅.22	0.1 - 0.4

[a] See Figure 4.3.

TABLE 4.16. Mean monthly methylmercury concentrations (ng/ℓ) for monitoring sites in the Wabigoon/English River system, July, 1979-June, 1980.

Site[a]	1979						1980					
	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun
1 Wabigoon Lake	.1	.1	.2*	.2	.2*	.1	.1	.1	.5	.1	.2	.2
4 Wabigoon River inflow to Wainwright Dam	.1	.1	.2*	.2	.2*	.1	.1	.1	.4	.3*	.2	.9
5 Wabigoon River outflow to Wainwright Dam	.1	.2	.2*	.1	.1*	.1	.1	.1	.4	.4*	.3	1.1
6 Wabigoon River at Minnitaki	.5	.4	.2*	.1	.1*	.1	.2	.1	.4	.6*	.8	1.7
2 Eagle River	.2	.2	.1	.6	.4*	.1	.1	.1	.2	.1	.2	.3
7 Wabigoon River inflow to Clay Lake	2.2	1.1	.3	1.2	1.2*	1.2	.3	.4	.3	.5	1.6	7.4
8 Clay Lake, eastern basin	2.1	1.0	.1	1.0	1.3*	1.5	.2	.4	.5	.3	2.5	4.1
9 Clay Lake, western basin	1.8	1.7	1.5	2.1	1.2*	.4	.3	.4*	.6	.6	.9	2.0
10 Wabigoon River, outflow of Clay Lake	1.5	1.7	1.3	1.7	1.2*	.8	.4	.5	.7	.6	1.9	1.4
11 Wabigoon River, inflow to Ball Lake	.4	.3	.6	1.1	1.6*	2.1	1.1	1.0	.4	1.3	.9	1.3
12 English River, inflow to Ball Lake	.1	.2	.2	.3	.3*	.4	.3	.1	.2	.5	.1	.2
13 English River, outflow to Ball Lake	.2	.1	.1	.1	.1*	.1	.4	.4	.1	.4	.3	.4

[a] See Figure 4.3.
N.B.: * = interpolated value.

TABLE 4.17. Methylmercury concentrations (ng/ℓ) in total effluent from the pulp and paper complex at Dryden.

Date	Grab Samples	Composite[a] Samples
Sep 27/78	1.0	
Aug 3/79	<0.2	
Oct 3/79	2.1	
Dec 19/79	0.3	<0.2
Jan 9/80	<0.2	<0.2
Feb 4/80	<0.2	<0.2
May 6/80		<0.2
Jun 4/80		0.5
Jun 11/80		0.4

[a] 24-hour composite - aliquots obtained every 15 minutes.

TABLE 4.18. Methylmercury concentrations (ng/ℓ) in grab samples of effluent from the Dryden sewage treatment plant[a].

Date (1979)	Concentration
Jun 12	0.4
Jun 20	0.3
Jul 4	0.5
Jul 18	0.7

[a] Utilizes conventional secondary treatment.

TABLE 4.19. Mean methylmercury concentrations (ng/ℓ) for monitoring sites in the Wabigoon/English River system for two study periods.

Site[a]	Aug/78-Jul/79[b]	Jul/79-Jun/80[b]	Mean for two periods
1 Wabigoon Lake	≅0.22	≅0.32	.27±.07
2 Eagle River		≅.18	
4 Wainwright Dam inflow	≅0.61	≅0.24	.43±.26
5 Wainwright Dam outflow	≅0.50	≅0.26	.38±.17
6 Minnitaki		≅0.44	
7 Clay Lake inflow	1.3	1.5	1.4±.14
8 Clay Lake eastern basin	1.4	1.2	1.3±.14
9 Clay Lake western basin - epilimnion	1.3	1.2	1.25±.07
10 Clay Lake outflow	1.3	1.3	1.30±0
11 Ball Lake inflow		1.0	

[a] See Figure 4.3.

[b] July, 1979 is included in both sets of data, since only 23 months of data are available for most sites.

TABLE 4.20. Mean methylmercury concentrations (ng/ℓ) in Clay Lake with and without the high values for June, 1980.

Site	Jul/79-Jun/80 (High values included)	Jul/79-May/80 (High values excluded)
Inflow	1.5	.94
Eastern basin	1.2	.99
Western basin	1.2	1.1
Outflow	1.3	1.3

TABLE 4.21. Correlation coefficients between methylmercury and flow, and between methylmercury and temperature.

Site	Temperature	Flow
2 Eagle River	.02/16/.94[a]	-.27/23/.20[a]
1 Wabigoon Lake	-.06/26/.79	
4 Inflow to Wainwright Dam[b]	.19/23/.39	-.10/23/.67
5 Outflow of Wainwright Dam[b]	.46/23/.03	-.04/23/.87
6 Minnitaki[b]	.47/16/.07	-.34/16/.02
7 Clay Lake, inflow	.70/63/.00	-.49/64/.00
8 Clay Lake Eastern Basin	.75/23/.00	
9 Clay Lake Western Basin	.64/22/.00	
10 Clay Lake outflow	.27/47/.04	-.22/48/.14
11 Wabigoon Inflow to Ball Lake	-.29/12/.35	

[a] Correlation coefficient/number of samples/probability.

[b] For non-high flow periods (see Section 2).

NOTE: Significant relationships are underlined.

TABLE 4.22. Methylmercury production as measured by fish in Jenkin's tubes, St. Clair River[a] at 15 C.

Site	Mercury in Sediments (μg/g)	Methylmercury Production μgMeHg/m²/day
Control Upstream	0.1	2.04
Outfall	15.6	1.88
0.4 mile	68.1	2.23
3 mile	6.4	2.76
8 mile	3.8	6.91
26 mile	0.1	0.77
Outfall Ditch	9.2	0.17

[a] Langley (1973).

TABLE 4.23. Methylmercury production as measured by fish in tubes[a] at 20°C.

Sediment Type[b]	Methylmercury Production (μgMeHg/m²/day)
1 Sand	13
2 Silt and Woodchips	15.7
3 Woodchips	3.9

[a] From Akagi, et al., 1979.

[b] All sediments had total mercury concentrations of 1 ppm.

TABLE 4.24. Methylmercury-total mercury relationships for water in the Wabigoon River system during non-high flows.

Site	Regression Equation	n	r	p
1 Wabigoon Lake	$y=0.010\ x+.11$	24	.63	<.001
4 Wainwright Dam inflow	$y=0.022\ x-.10$	21	.62	<.01
5 Wainwright Dam outflow	$y=0.019\ x+.03$	21	.61	<.01
7 Clay Lake inflow	$y=0.055\ x-.27$	59	.75	<.001
8 Clay Lake, eastern basin	$y=0.043\ x-.49$	18	.70	<.001
9 Clay Lake, western basin	$y=0.055\ x+.31$	21	.52	<.01
10 Clay Lake outflow	$y=0.051\ x+.66$	46	.44	<.01
11 Wabigoon River inflow to Ball Lake	$y=0.064\ x+.21$	10	.72	<.01

[a] See Figure 4.3.

n = Number of values.

r = Correlation coefficient.

p = Probability.

y = Regression equation.

TABLE 4.25. Multi-linear regression analysis of methylmercury on total mercury and temperature.

Site[a]	n	% of methylmercury variance explained by total mercury concentrations	% of residual variance explained by temperature	% total variance explained
1 Wabigoon Lake	22	39	0	39
4 Wainwright Dam[b] inflow	20	39	2	41
5 Wainwright Dam[b] outflow	20	37	4	41
6 Minnitaki[b]	13	5	21	26
7 Clay Lake inflow	58	55	4	59
8 Clay Lake, eastern basin	17	51	6	57
9 Clay Lake, western basin - epilimnion	19	25	24	49
10 Clay Lake outflow	44	19	2	21
11 Ball Lake inflow	10	52	0	52

[a] See Figure 4.3.

[b] Non-high flow periods (see Section 2).

TABLE 4.26. Multi-linear regression analysis of methylmercury on total mercury, temperature, flow and suspended solids, inflow to Clay Lake.

Period[a]	m	% of methylmercury variance explained by total mercury	% of residual variance explained by temperature	% of residual variance explained by flow	% of residual explained by Suspended Solids	% total variance explained
1 Non-high flow	40	55	1	5	-	61
2 Non-high flow	20	59	1	1	0	61
3 High flow	13	37	1	0	-	38
4 Complete study period (all data)	58	57	4	3	-	64
5 Complete study period	28	70	1	4	0	75

[a] See Section 2.

TABLE 4.27. Total mercury concentrations (ng/ℓ) in duplicate samples from Dryden to Clay Lake, May 5-June 24, 1980.

Site[a]	May 5-6	May 20-21	June 2-3	June 5	June 9-10	June 16-17	June 23-24
2 Eagle River	2.5	2.5	4.2±2.5	6.0±5.4	8.0		12.0±5.6
1 Wabigoon Lake	2.5	11.0±11.0	2.5		3.8±1.8	24.0±11.3	36.5±29.0
4 Inflow to Wainwright Dam	34.5±0.7	43.5±2.1	40.0±5.6		2.5	54.0±1.4	46.5±17.7
5 Outflow of Wainwright Dam	31.5±0.7	26.0±2.8	26.0±5.6		5.8±4.6	33.5±0.7	68.5±4.9
6 Wabigoon River at Minnitaki	40.5±0.7	19.0±0.0	28.5±7.8	140.0±14.1	40.0±1.4	28.0±0.0	72.5±2.1
6A Wabigoon River upstream of confluence of Eagle River	46.0±0.0	23.5±3.5	9.5±0.7	38.0±2.8	39.0±2.8	165.5±105.4	62.0±4.2
6B Wabigoon River 3.1 km downstream of confluence of Eagle River	22.0±0.0	24.0±1.4	10.0±0.0	28.0±0.0	11.0±0.0	445.0±360.6	57.0±17.0
6C Wabigoon River 3.1 km downstream of confluence of Eagle River	26.0±1.4	23.5±3.5	22.0±7.1	31.0±7.1	46.0±7.1	120.0±0.0	52.0±17.0
6D Wabigoon River at Highway #105	13.5±2.1	22.5±0.7	45.0±8.5	35.0±8.5	44.5±3.5	71.0±8.5	144.5±106.8
7 Wabigoon River inflow to Clay Lake	29.5±6.4	29.0±0.0	42.5±2.1	50.0±2.8	48.0±3.5	88.5±30.4	42.5±0.7

[a] See Figure 4.56.

TABLE 4.28. Methylmercury concentrations (ng/ℓ) in the Wabigoon River, Dryden to Clay Lake, May 5-June 24, 1980.

Site[a]	May 5-6	May 20-21	June 2-3	June 5	June 9-10	June 16-17	June 23-24
1 Wabigoon Lake	0.1	0.3	0.1		0.1	0.2	0.3
2 Eagle River	0.2		0.1	0.4	0.1		
4 Inflow to Wainwright Dam	0.2		0.5		0.5		1.7
5 Outflow of Wainwright Dam	0.3		1.0		0.5		1.9
6 Wabigoon River at Minnitaki Road	0.8		0.3	0.4	1.2		4.8
6A Wabigoon River upstream of confluence of Eagle River	1.4	1.4	0.1	0.1	1.0	0.6	0.5
6B Wabigoon River 3.1 km downstream of confluence of Eagle River	1.1	1.3	0.2	0.1	0.4	0.4	0.1
6C Wabigoon River 9.8 km downstream of confluence of Eagle River	1.4	1.1	0.4	0.2	0.2	0.8	0.1
6D Wabigoon River at Highway #105	1.1	1.5	1.9	2.3	1.0		2.6
7 Wabigoon River inflow to Clay Lake	1.6	1.9	2.4	3.5	3.8	9.4	18.0

[a] See Figure 4.56.

TABLE 4.29. Methylmercury loadings (kg) for the Wabigoon River system, July, 1979-June, 1980.

Site[a]	Loading	Monthly Range
1 Wabigoon Lake	≅0.05(0.026-0.072)	0.001-0.015
4 Inflow to Wainwright Dam	≅0.06(0.047-0.079)	0.002-0.013
5 Outflow of Wainwright Dam	≅0.07(0.048-0.085)	0.002-0.014
6 Minnitaki	.19	0.003-0.016
2 Eagle River	≅0.07(0.039-0.095)	0.002-0.018
7 Inflow to Clay Lake	1.1	0.02-0.20
10 Outflow of Clay Lake	1.3	0.03-0.14
11 Inflow to Ball Lake	1.4	0.03-0.31
12 English River inflow to Ball Lake	≅3(2.5-3.5)	0.05-0.66
13 English River outflow of Ball Lake	≅3(2.3-3.7)	0.06-0.62

[a] See Figure 4.3.

TABLE 4.30. Correlation coefficients between total mercury and other parameters under non-high flow conditions.

Site	pH	Conductivity	Cl[a]	SO_4	Na	Fe	Mn	S.S.	Turb.	T.P.
Eagle River	-.12[b] 28[c] .54[d]	.11 28 .56	-.15 12 .65	-.26 13 .39	-.09 13 .76	-.29 10 .41	-.24 9 .53	-.32 12 .30	-.41 10 .24	-.64 4 .37
Wabigoon Lake	.22 24 .30	.01 28 .62	.32 14 .28	-.01 19 .97	.74 19 .00	.53 9 .14	.42 8 .31	.18 18 .48	.28 9 .46	-.39 11 .23
Inflow to Wainwright Dam	-.22 24 .31	.07 28 .73	.49 14 .08	-.00 19 1.0	.15 19 .55	.18 9 .65	.79 8 .02	.20 18 .42	.58 9 .10	.42 11 .20
Outflow of Wainwright Dam	-.28 24 .18	.09 28 .65	.31 14 .28	.02 19 .92	.13 18 .63	.04 9 .92	.17 8 .69	.22 18 .38	.21 9 .58	10 11 .77
Minnitaki	-.11 24 .63	.62 29 .00	.70 11 .02	.44 12 .16	.78 12 .00	.32 10 .38	.76 9 .02	.03 11 .94	.63 10 .05	.88 3 .31
Clay Lake Inflow	.19 23 .38	-.48 24 .02	.01 9 .99	-.47 27 .01	-.20 26 .33	.74 8 .04	.70 8 .06	.61 23 .00	.82 9 .01	.51 17 .04
Eastern Basin	.41 23 .00	-.61 26 .00	-.11 12 .38	-.18 24 .20	-.00 23 .49	.48 12 .08	-.33 6 .26	.53 21 .01	-.65 7 .06	.35 16 .09
Western Basin	.44 27 .02	-.26 29 .17	.24 7 .60	.08 27 .70	-.11 25 .60	.27 7 .55	.34 7 .46	-.18 24 .38	.27 8 .52	-.53 19 .02
Clay Lake Outlet	.26 28 .17	-.45 31 .01	.26 11 .43	-.29 26 .15	.14 27 .49	-.12 9 .75	-.17 8 .69	-.07 25 .73	-.00 9 .99	.44 18 .07
Inflow to Ball Lake	-.43 9 .25	.43 10 .22	.55 9 .12	.54 9 .13	.45 8 .26	.62 9 .07	.00 8 1.0	-.02 8 .97	.38 9 .32	

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[a] Cl = Chloride, SO_4 = Sulphate, Na = Sodium, Fe = Iron, Mn = Manganese, S.S. = Suspended Solids, Turb. = Turbidity, T.P. = Total Phosphorus.

[b] Correlation coefficient.

[c] Number of samples.

[d] Probability.

NOTE: Statistically significant relationships are underlined.

TABLE 4.31. Correlation coefficients betweem methylmercury and other parameters under non-high flow conditions.

Site	pH	Conductivity	Cl[a]	SO_4	Na	Fe	Mn	S.S.	Turb.	T.P.
Eagle River	.09[b]	-.20	-.05	.12	-.11	-.86	.77	.94	-.41	.69
	27[c]	22	10	11	11	8	7	10	10	4
	.70[d]	.38	.90	.73	.74	.00	.04	.00	.24	.31
Wabigoon Lake	.43	.12	.3	.09	.53	.22	.39	.61	.56	-.03
	19	23	13	17	17	9	8	16	9	9
	.07	.58	.30	.74	.03	.57	.34	.01	.12	.94
Inflow to	.04	.01	.08	.46	.10	-.13	.92	-.26	.90	.37
Wainwright Dam	19	19	12	16	16	8	7	15	8	9
	.88	.96	.80	.08	.72	.76	.00	.35	.00	.33
Outflow of	-.09	.44	.63	.92	.53	.18	.92	.66	.92	.61
Wainwright Dam	18	20	13	16	15	9	8	15	9	8
	.72	.05	.02	.00	.04	.64	.00	.00	.00	.11
Minnitaki	.44	.55	-.17	-.26	-.38	.17	.11	.89	-.01	-.36
	12	14	10	11	11	9	8	10	9	3
	.16	.04	.64	.45	.25	.67	.79	.00	.98	.77
Clay Lake	.18	-.21	.14	-.38	-.11	.83	.78	.57	.78	.29
Inflow	23	23	9	27	26	8	8	23	9	17
	.22	.22	.36	.08	.29	.00	.01	.00	.00	.12
Eastern	.46	-.74	.17	-.24	-.49	-.20	-.37	.12	.23	.82
Basin	17	16	11	18	18	11	5	16	6	12
	.03	.00	.31	.17	.02	.28	.26	.48	.32	.03
Western	.66	-.37	-.52	-.18	-.17	.16	.20	-.35	-.46	-.52
Basin	19	18	6	19	17	6	6	17	7	13
	.00	.06	.14	.23	.25	.38	.35	.09	.84	.03
Clay Lake	.31	-.33	.01	-.30	-.27	-.10	.38	-.15	-.14	-.64
outflow	26	27	10	24	25	8	7	24	8	18
	.12	.09	.97	.16	.19	.82	.40	.48	.75	.00
Ball Lake	-41	.25	.36	.41	.17	.78	-.04	-.80	.29	
inflow	10	11	10	10	9	10	9	9	10	
	.24	.46	.30	.24	.65	.00	.92	.85	.41	

[a] Cl = Chloride, SO_4 = Sulphate, Na = Sodium, Fe = Iron, Mn = Manganese, S.S. = Suspended Solids, Turb. = Turbidity, T.P. = Total Phosphorus.

[b] Correlation coefficient.

[c] Number of samples.

[d] Probability.

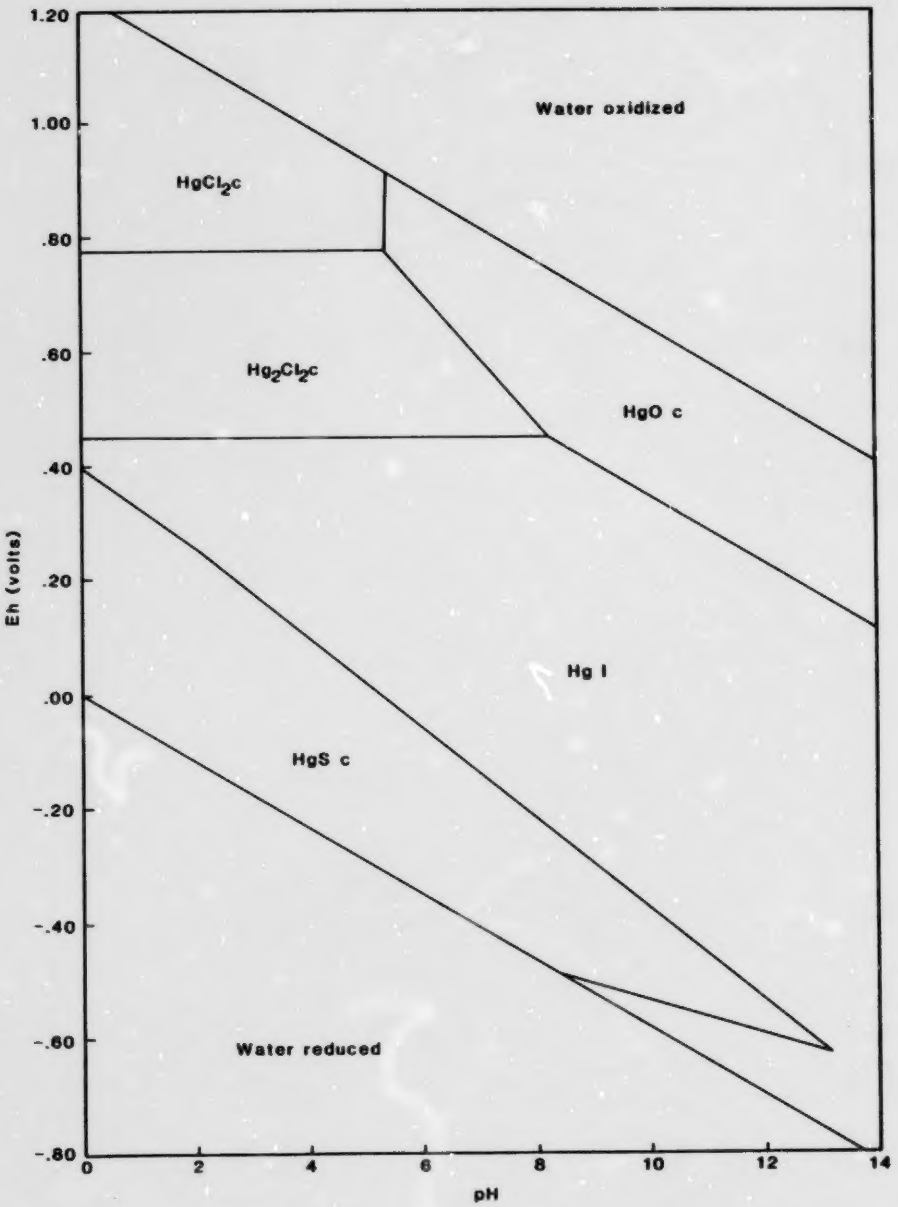


Figure 4.1 Fields of stability for solids (c) and liquid (l) mercury species at 25°C and 1 atmosphere pressure. System includes water containing 36 ppm Cl–, total sulfur 96 ppm as SO_4. From Hem (1970).

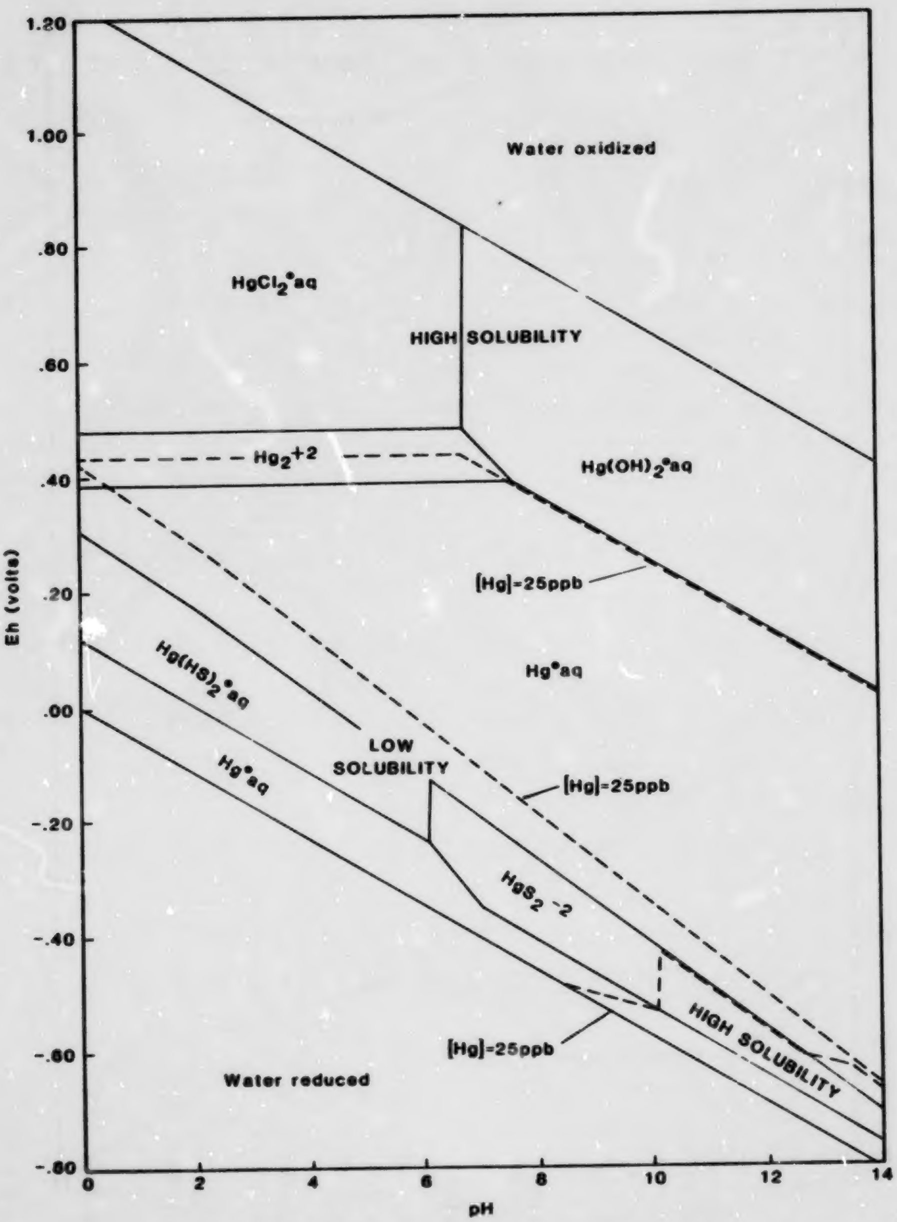
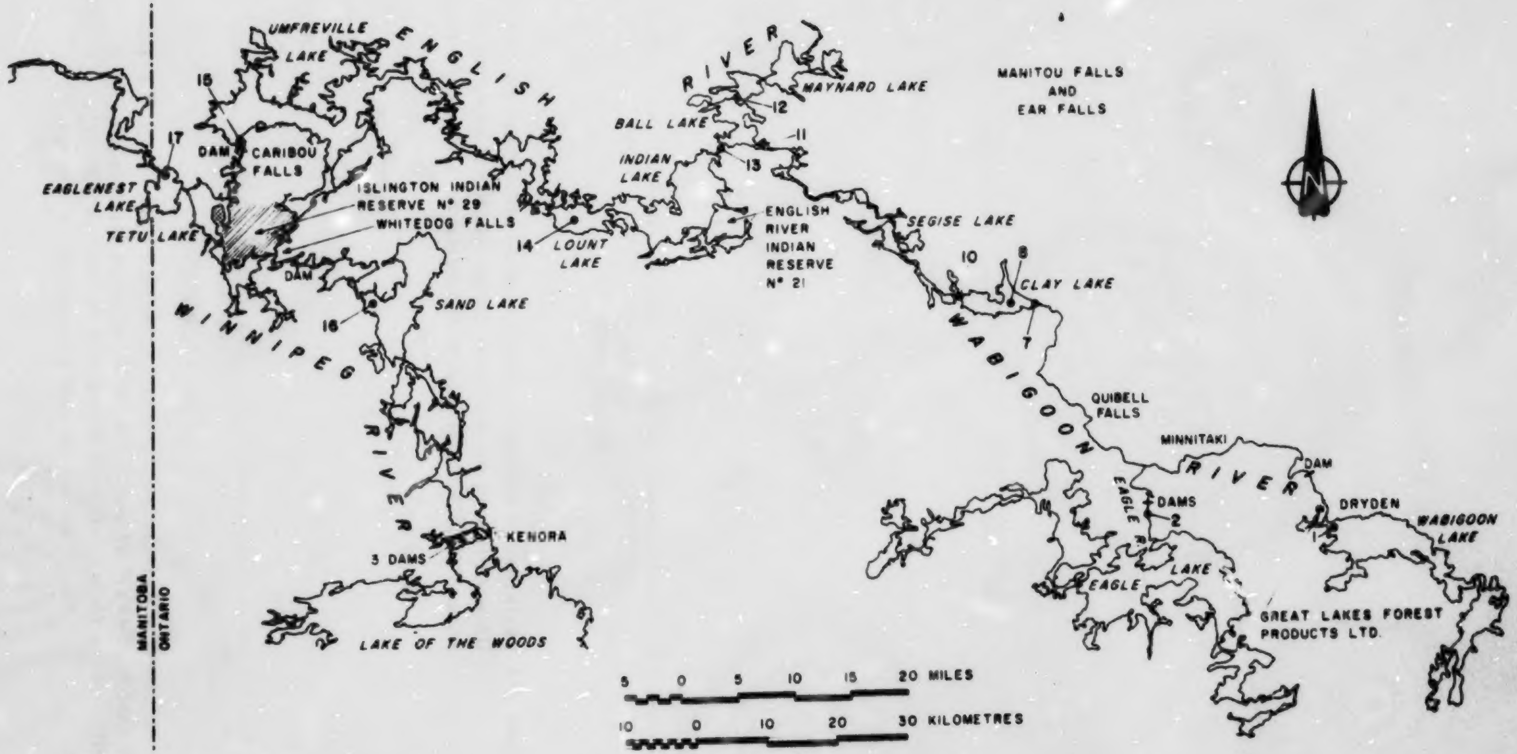


Figure 4.2 Fields of stability for aqueous mercury species at 25°C and 1 atmosphere pressure. System includes water containing 36 ppm Cl^-, total sulfur 96 ppm as sulfate. Dashed line indicates approximate solubility of mercury in this system. From Hem (1970.).


UMFREVILLE LAKE
ENGLISH RIVER
MAYNARD LAKE
MANITOU FALLS AND EAR FALLS
15
17
DAM
CARIBOU FALLS
BALL LAKE
12
11
13
INDIAN LAKE
EAGLENEST LAKE
TETU LAKE
ISLINGTON INDIAN RESERVE Nº 29
WHITEDOG FALLS
14
LOUNT LAKE
ENGLISH RIVER INDIAN RESERVE Nº 21
SEGISE LAKE
10
8
CLAY LAKE
7
DAM
SAND LAKE
16
WINNIPEG RIVER
WABIGOON RIVER
QUIBELL FALLS
MINNITAKI
DAM
DRYDEN
WABIGOON LAKE
1
DAMS
2
EAGLE R
EAGLE LAKE
KENORA
3 DAMS
LAKE OF THE WOODS
GREAT LAKES FOREST PRODUCTS LTD.
MANITOBA
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5 0 5 10 15 20 MILES
10 0 10 20 30 KILOMETRES

Figure 4.3 Sampling sites in the Wabigoon/English/Winnipeg River System.

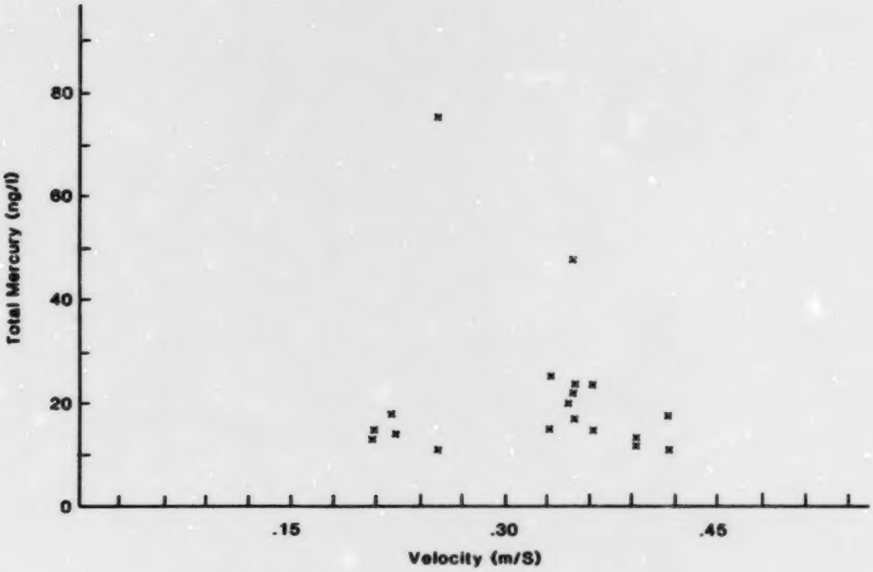


Figure 4.4 Variation of mercury concentration with mean velocity. Data obtained by intensive cross sectional sampling on August 23, 1978, at site 4, the inflow to Wainwright Dam.

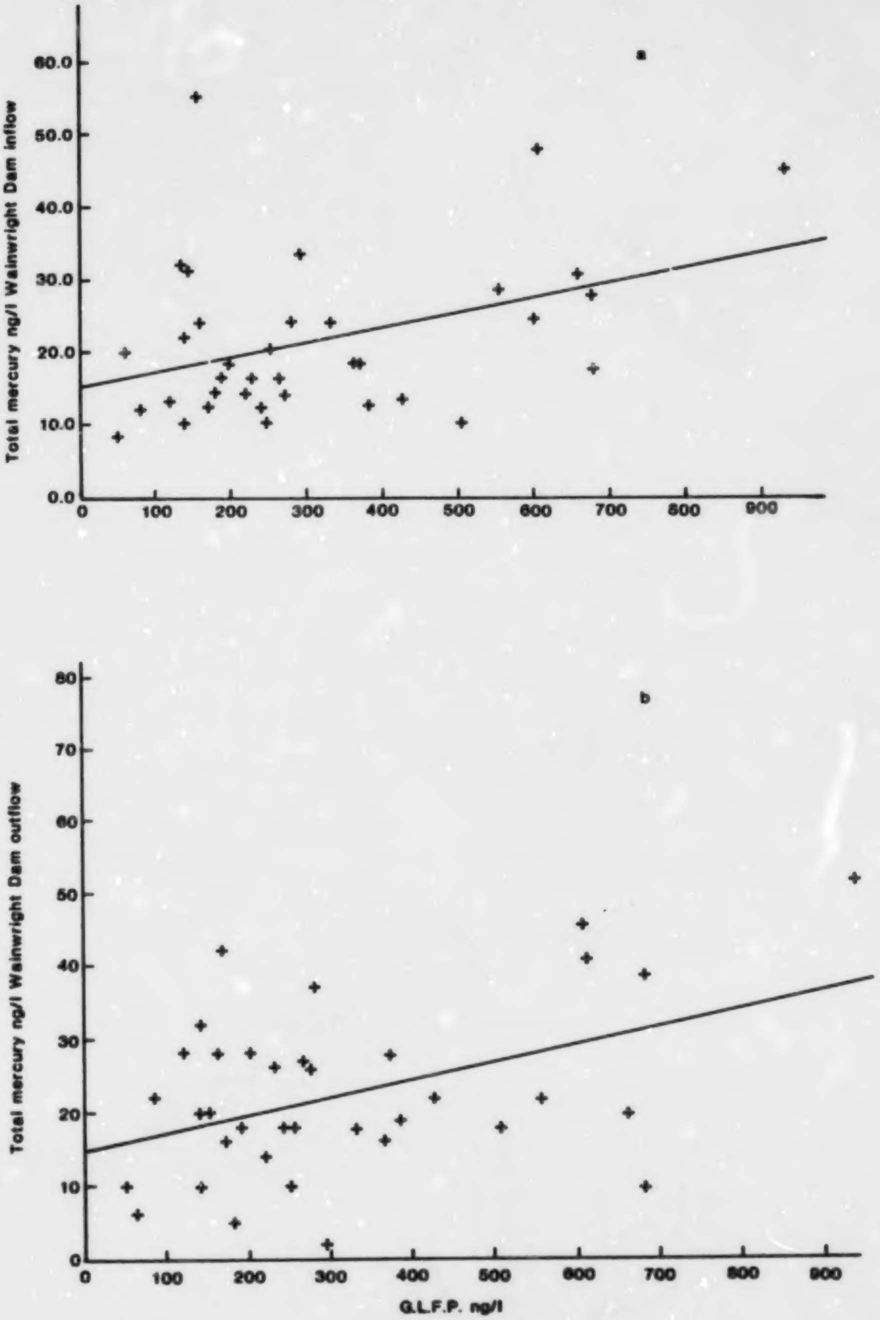


Figure 4.5 Relationships between mercury concentration in industrial effluent and in water at (a) the inflow to Wainwright Dam and (b) the outflow of Wainwright Dam. (a) $r=.42$ $p<.05$, the outflow of Wainwright Dam (b) $r=.48$ $p<.05$.

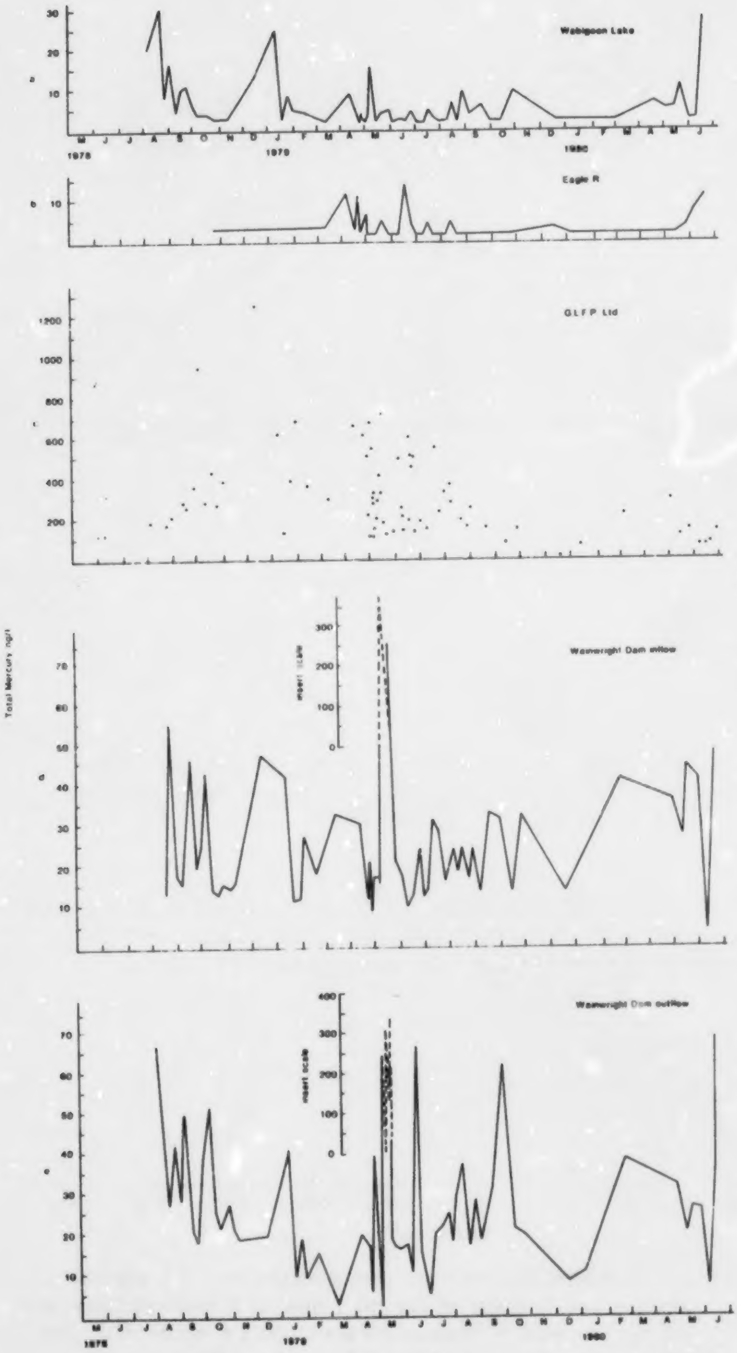
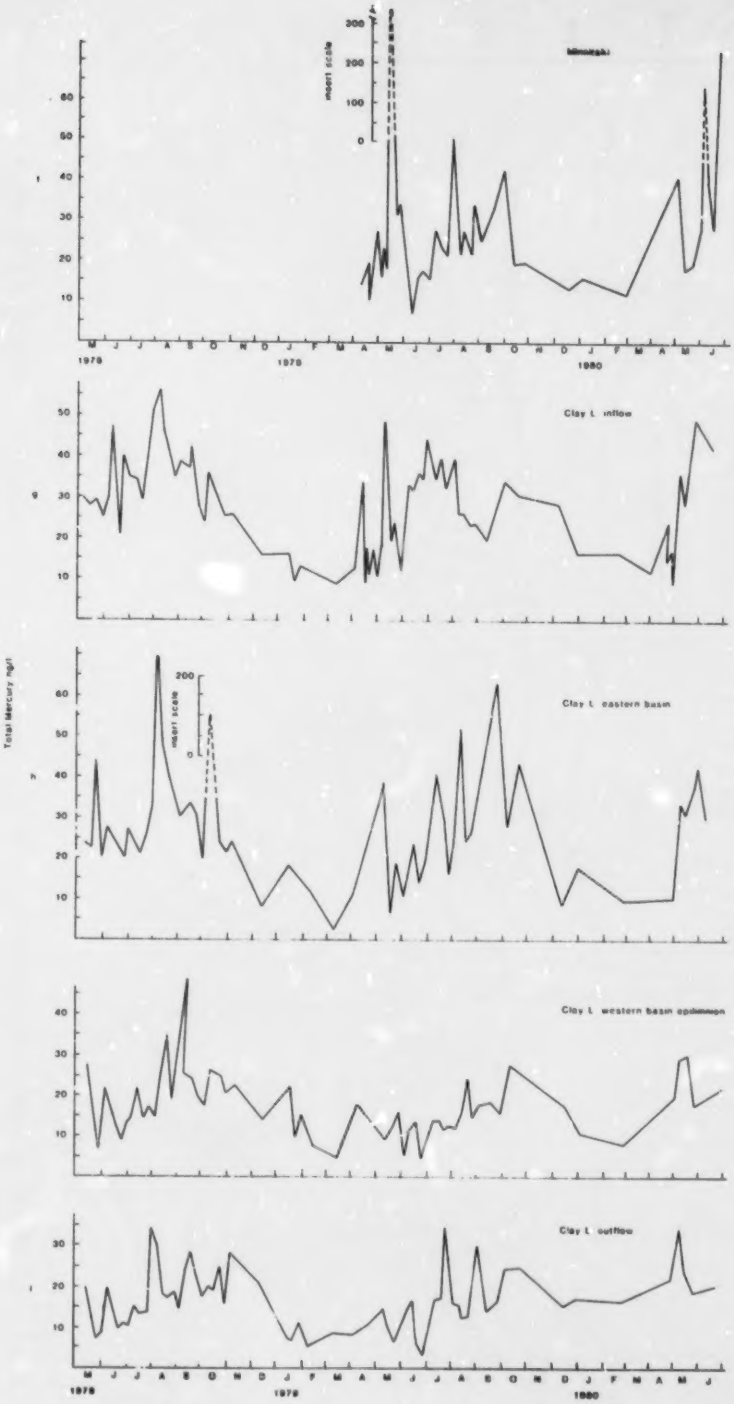


Figure 4.6 Mercury concentrations in water from selected sites on the Wabigoon River system.



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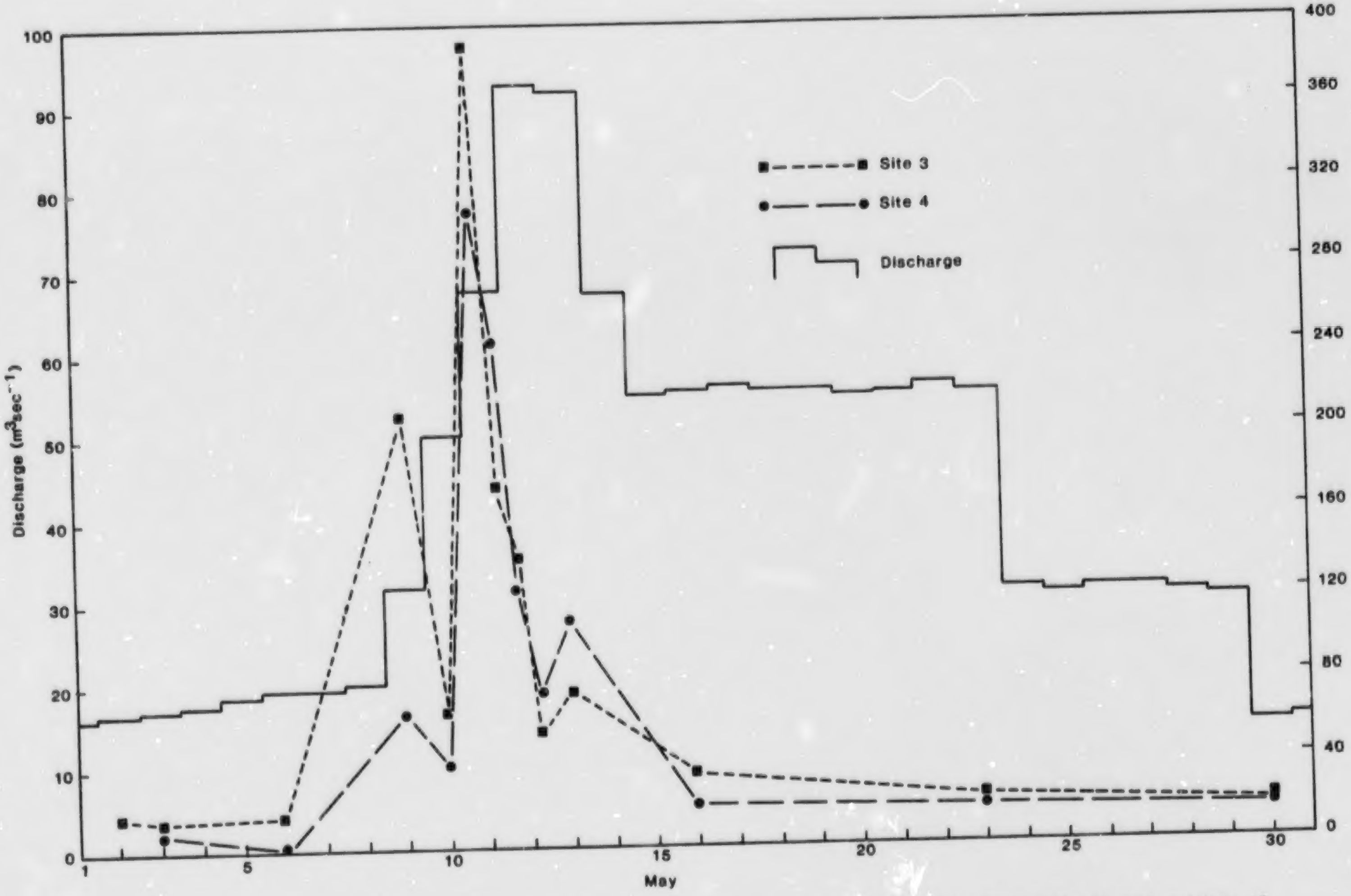


Figure 4.7 Mercury concentrations and controlled discharges at the inflow to Wainwright Dam (site 4) and outflow of Wainwright Dam (site 5) during controlled spring flush, May, 1979.

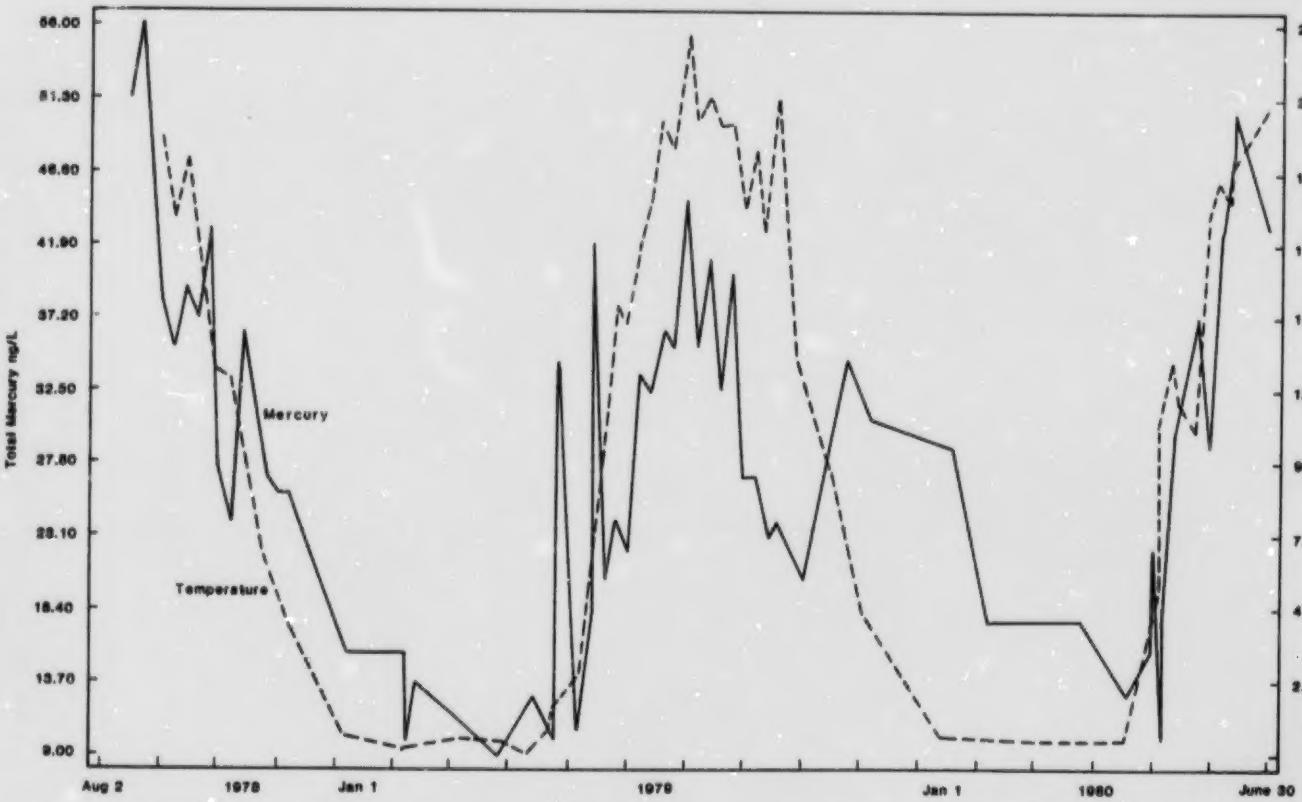


Figure 4.8 Mercury concentrations and water temperature Wabigoon River inflow to Clay Lake (Site 7) Aug 1978-June 1980

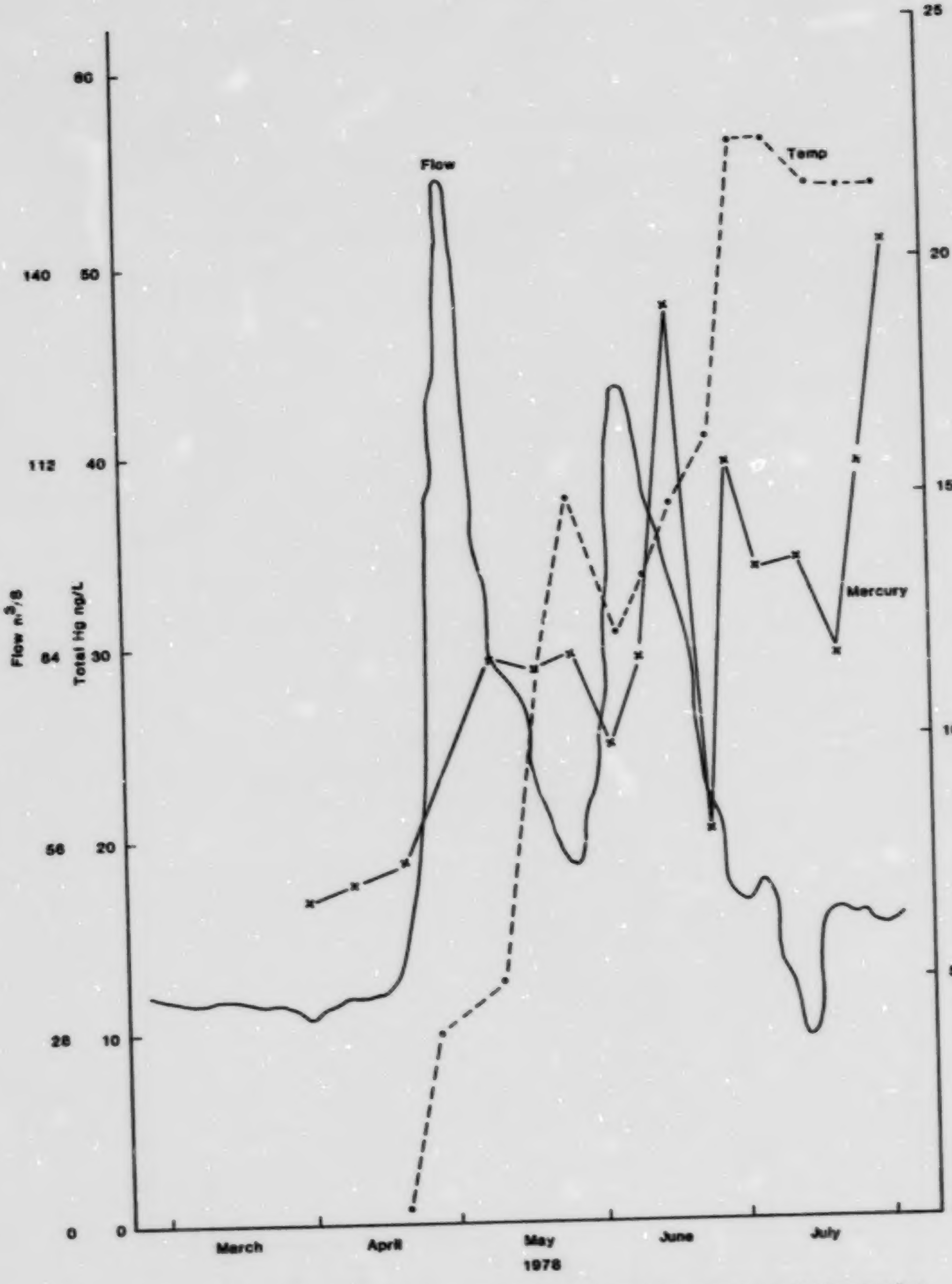


Figure 4.9 Mercury concentrations, river flow and temperature during spring runoff, 1978, Wabigoon River inflow to Clay Lake.

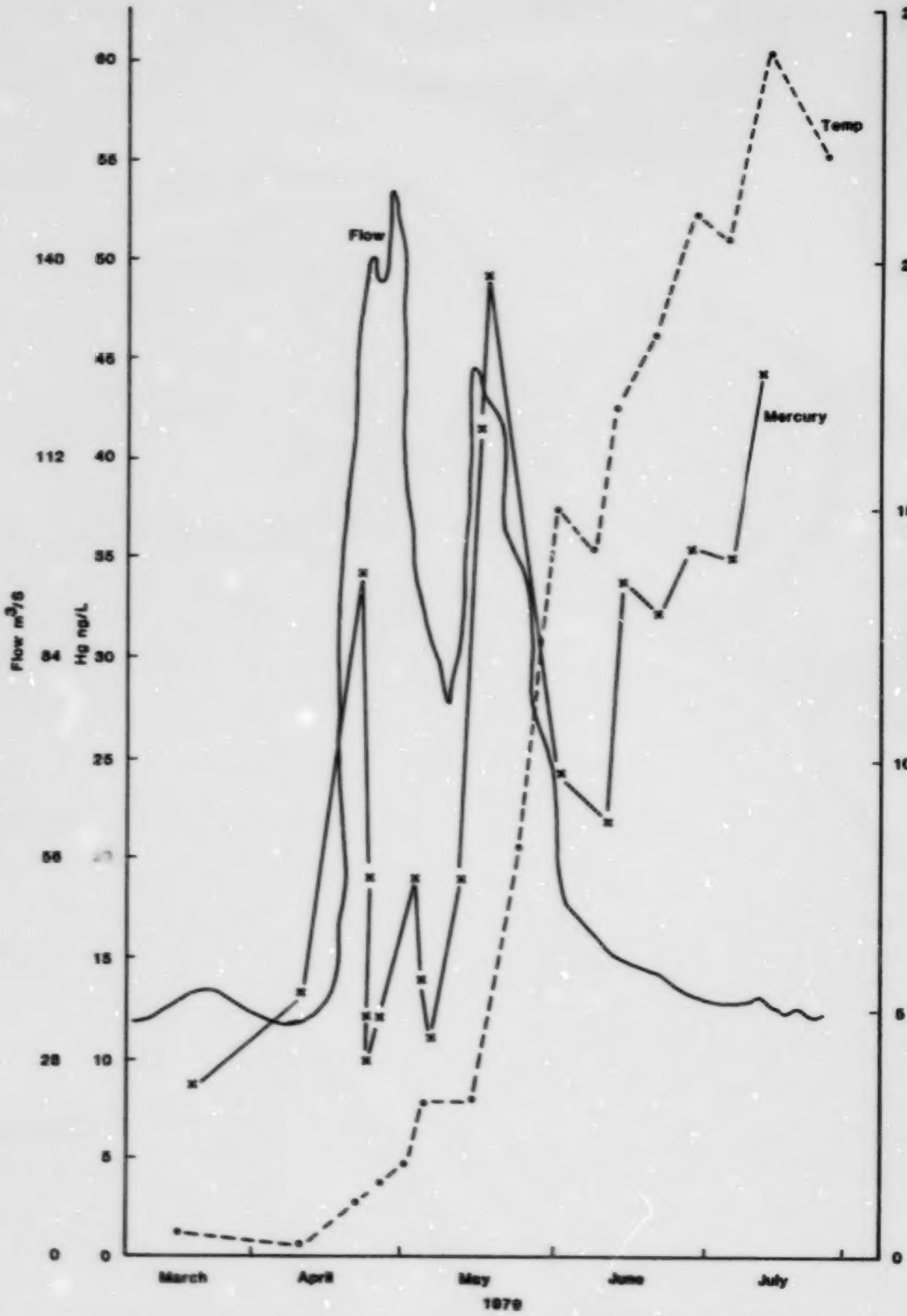


Figure 4.10 Mercury concentrations, river flow and temperature, Wabigoon River inflow to Clay Lake during spring runoff, 1979, Wabigoon River inflow to Clay Lake.

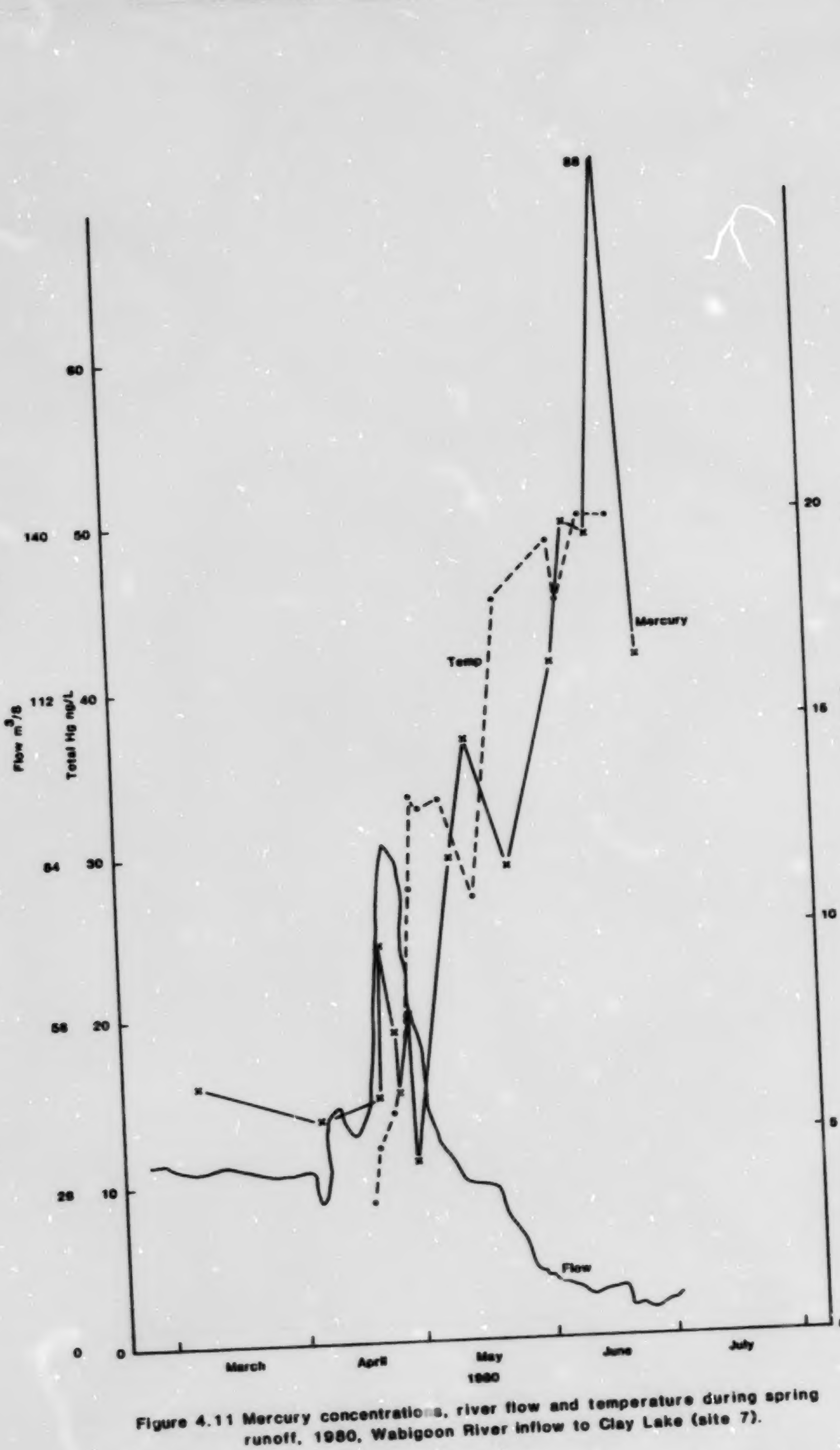


Figure 4.11 Mercury concentrations, river flow and temperature during spring runoff, 1980, Wabigoon River inflow to Clay Lake (site 7).

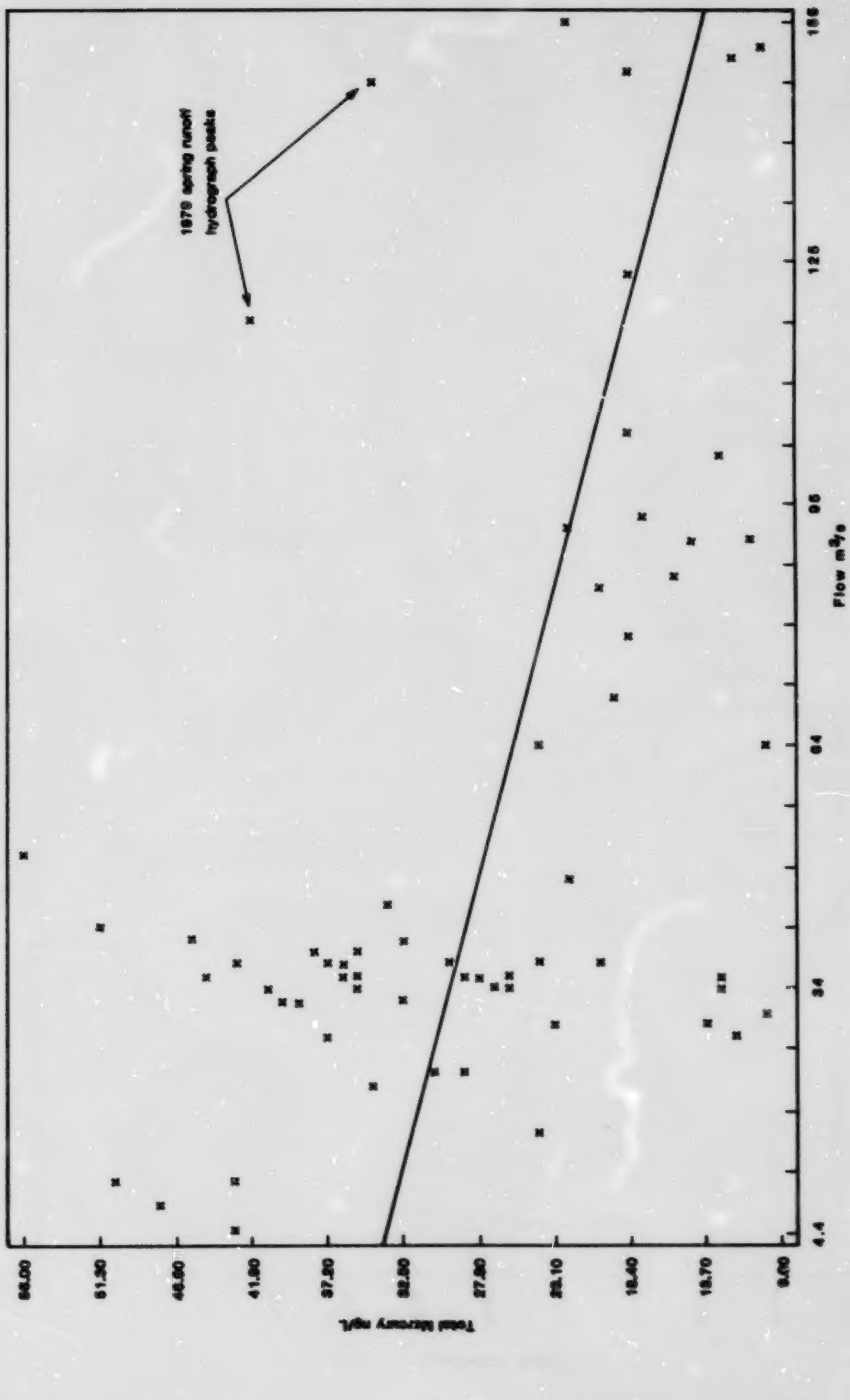


Figure 4.12 Relationship between Mercury concentrations and flow Wabigoon R. inflow to Clay Lake. Atypical high flow mercury values correspond to spring runoff peaks (Fig.4.10)

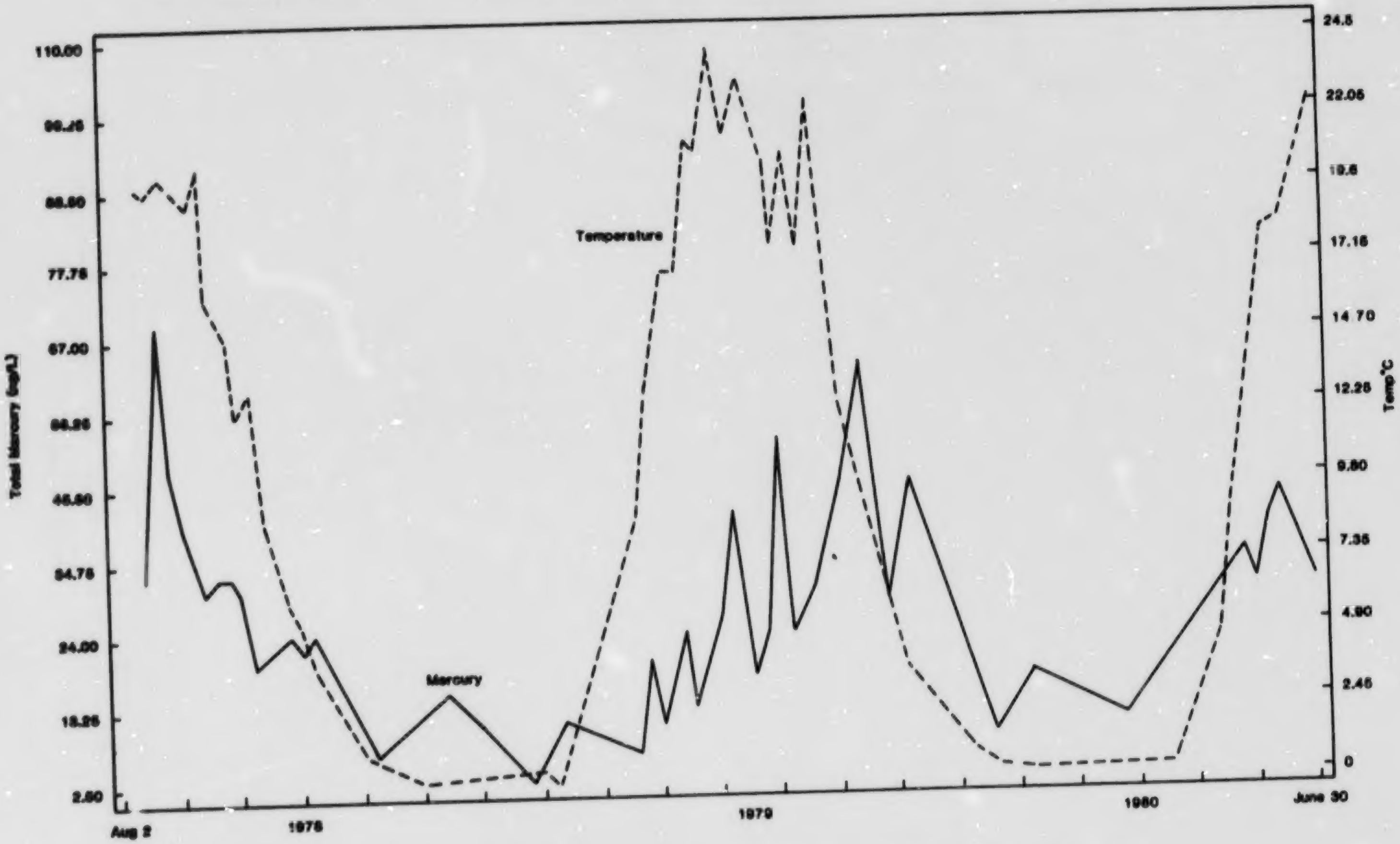


Figure 4.13 Mercury concentrations and temperatures, Clay Lake eastern basin (site 8), August 1978 to June 1980.

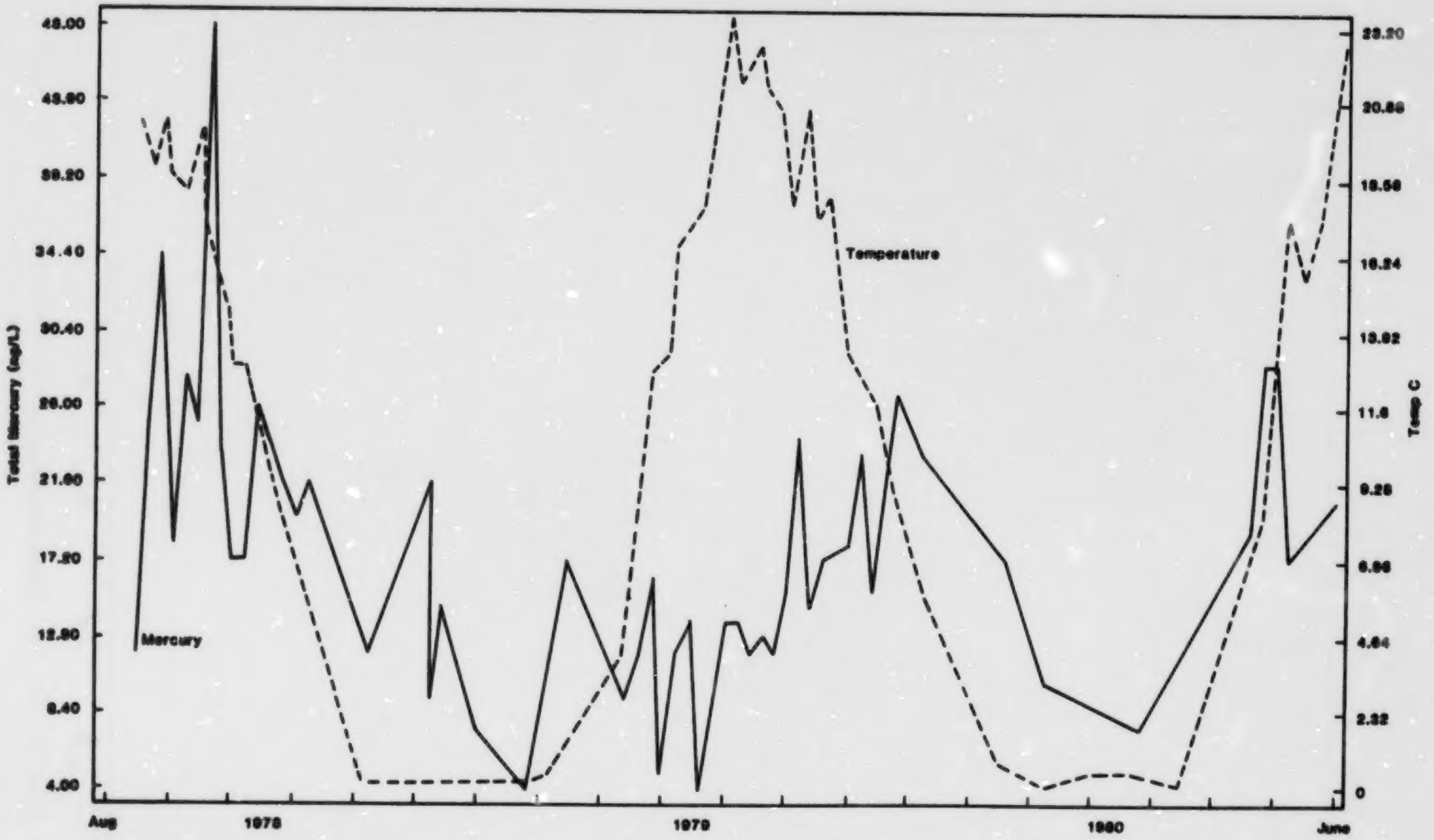


Figure 4.14 Mercury concentrations and Temperatures, Clay Lake, western basin epilimnion (site 9) August 1978 to June, 1980.

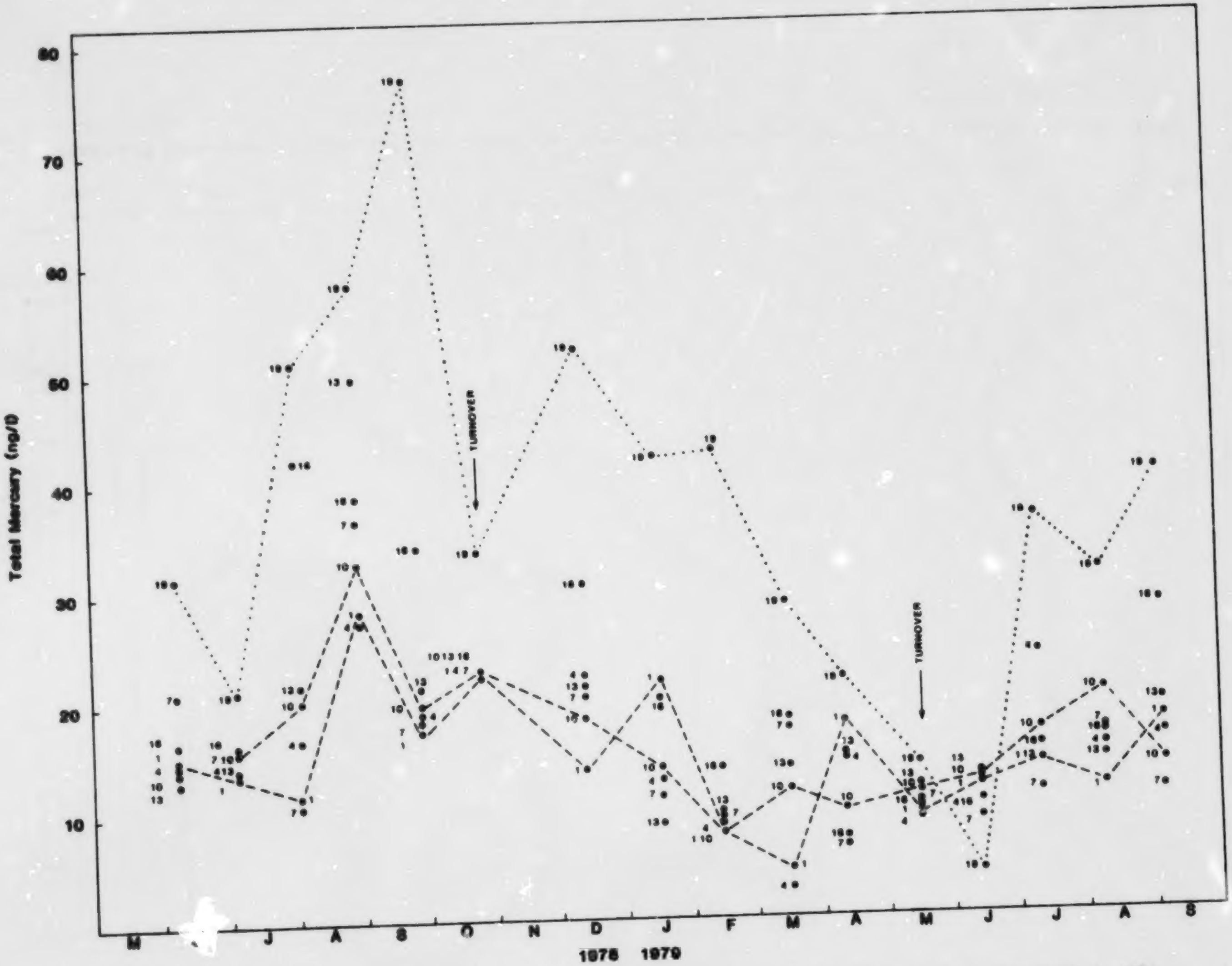


Figure 4.15 Distribution of total mercury in the western basin of Clay Lake (site 9) at designated depths below lake surface.

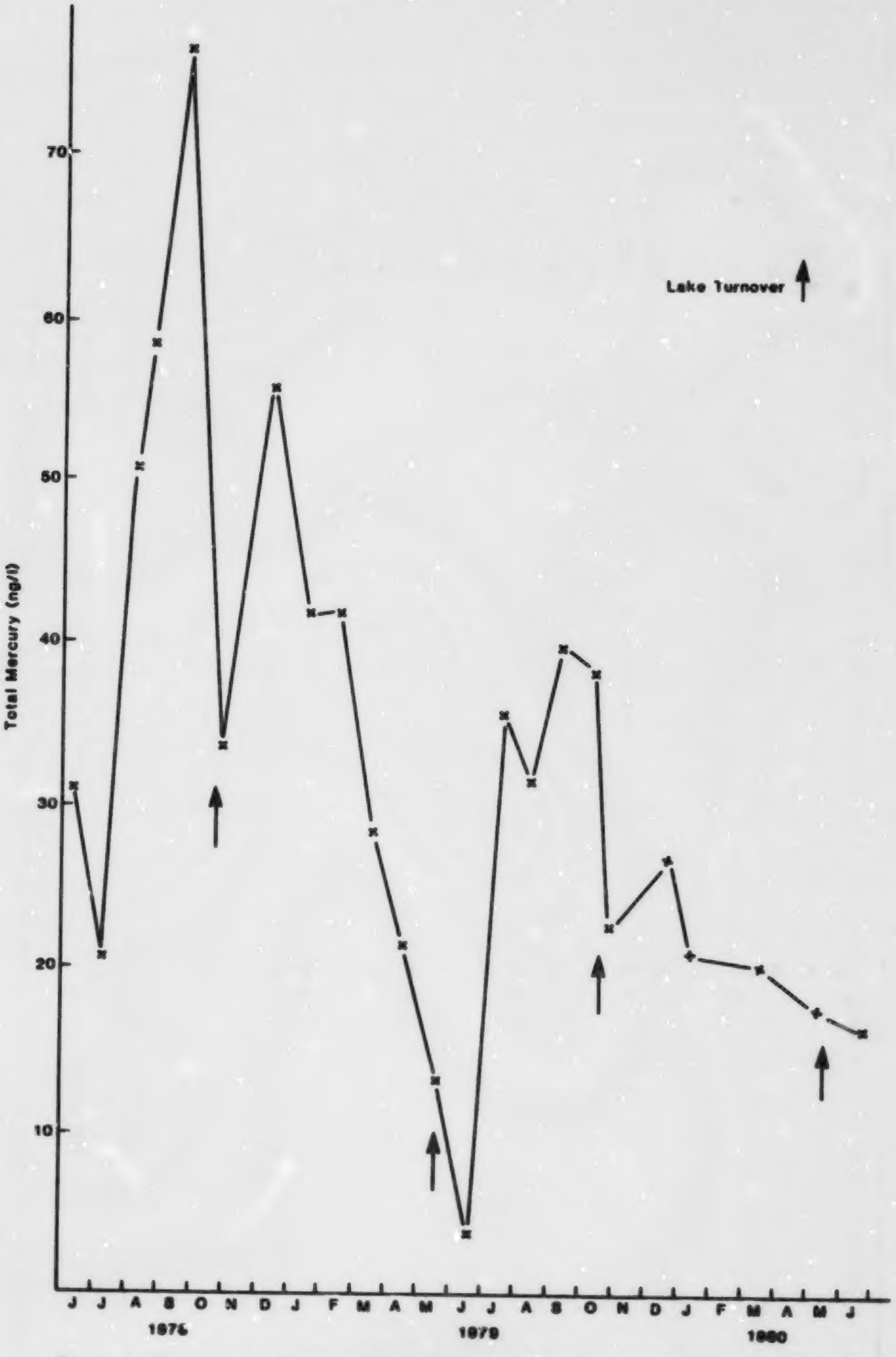


Figure 4.16 Mercury concentrations Clay Lake western basin, (site 9) 1m above bottom June 1978-June 1980.

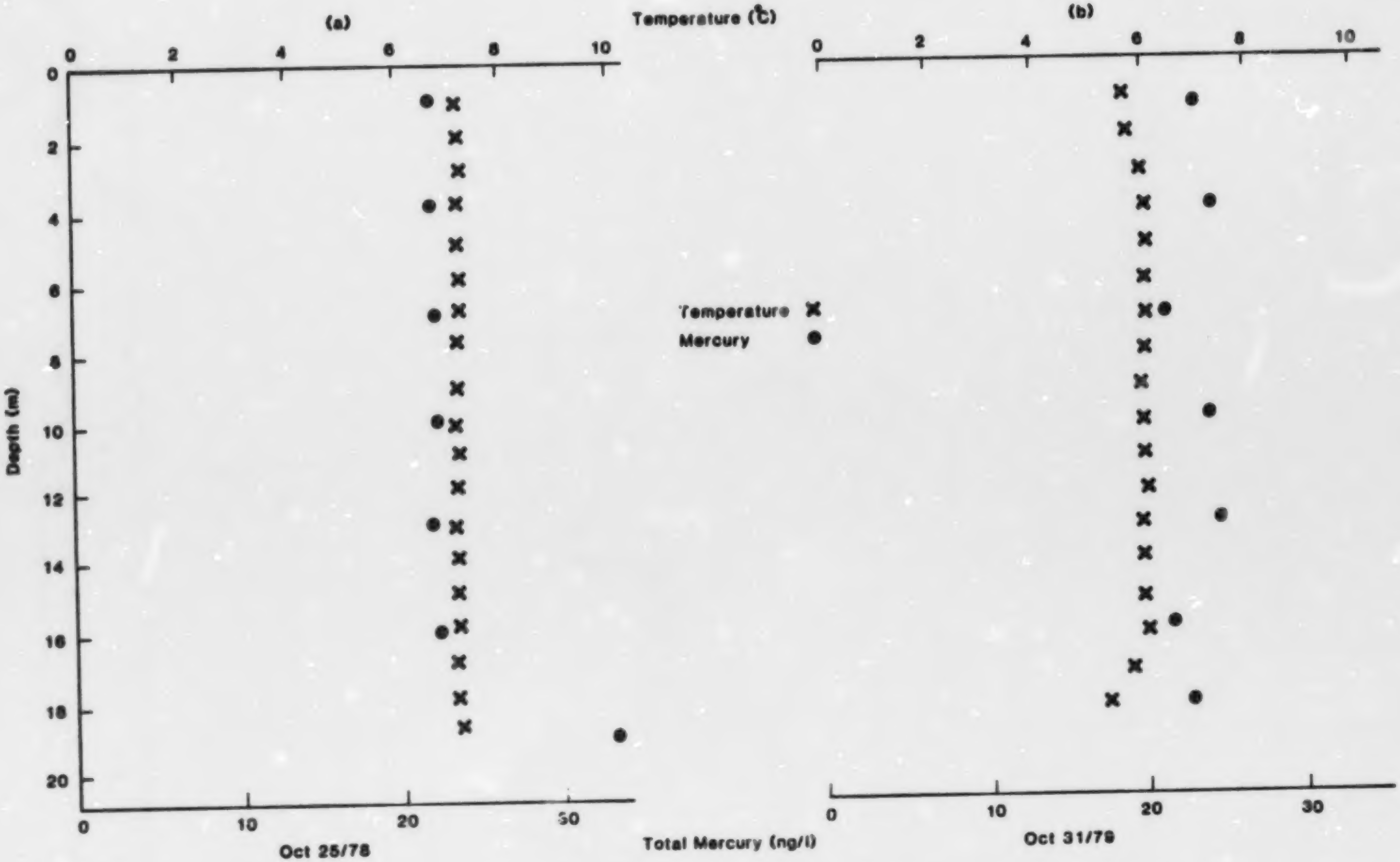


Figure 4.17 Mercury profiles of western basin of Clay Lake (site 9) fall turnover (a) 1978, (b) 1979.

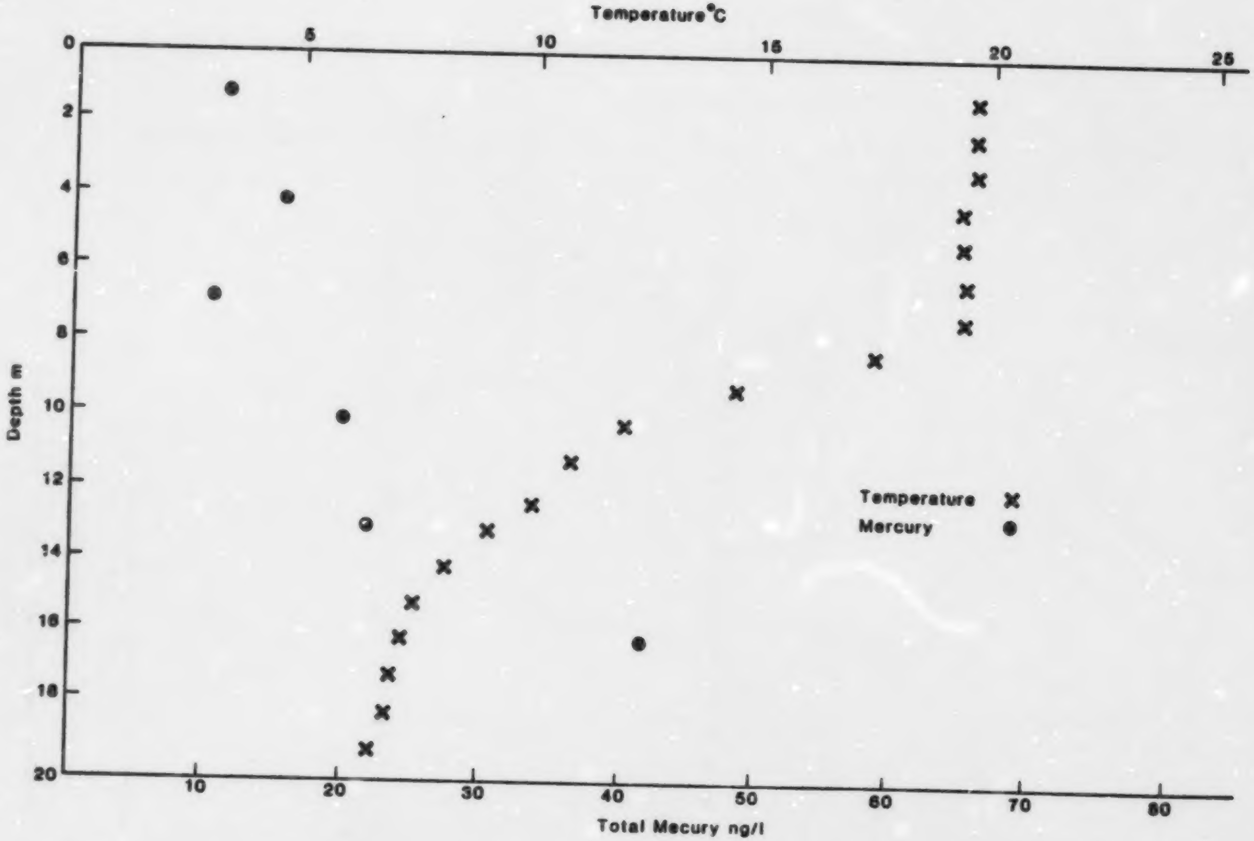


Figure 4.18 Mecury profile of western basin of Clay Lake (site 9) on Aug. 2, 1978.

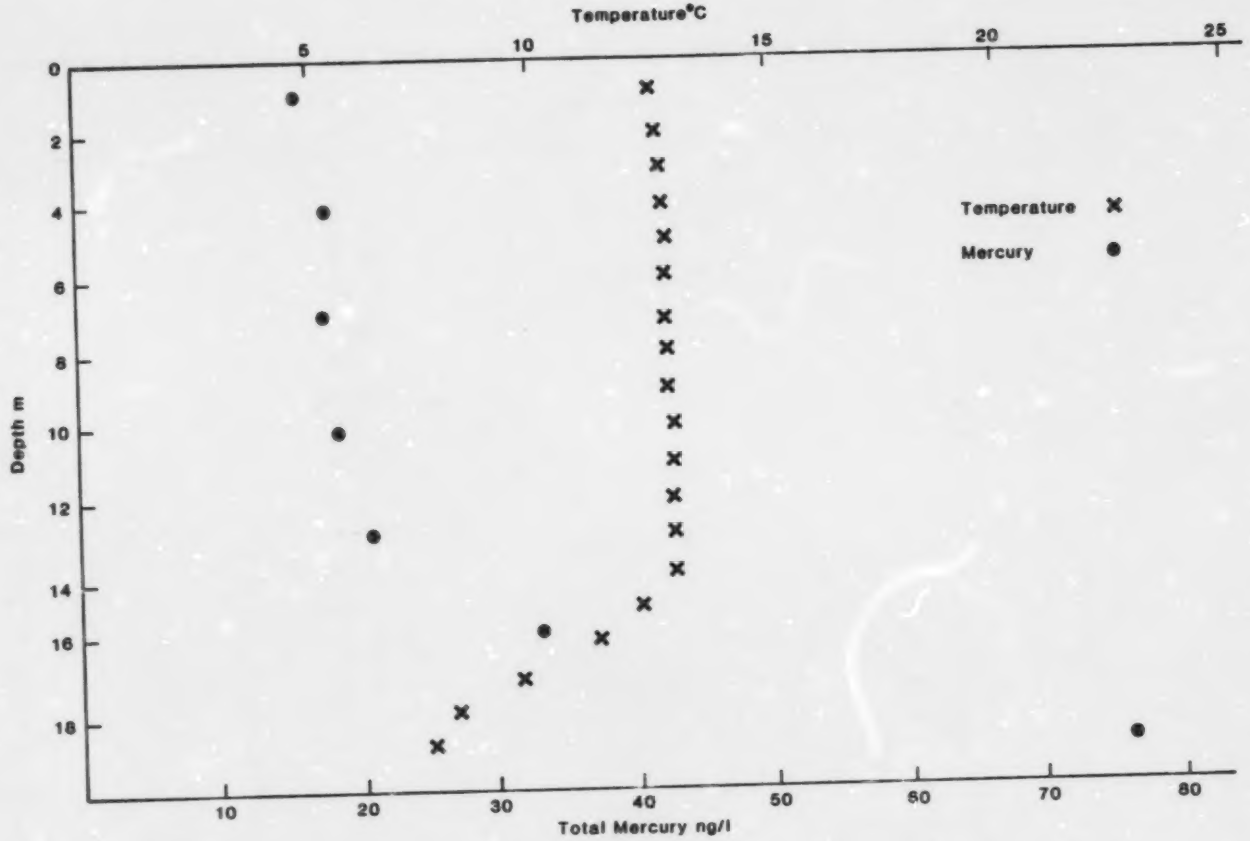


Figure 4.19 Mercury profile of western basin of Clay Lake (site 9) Sept 27,1978.

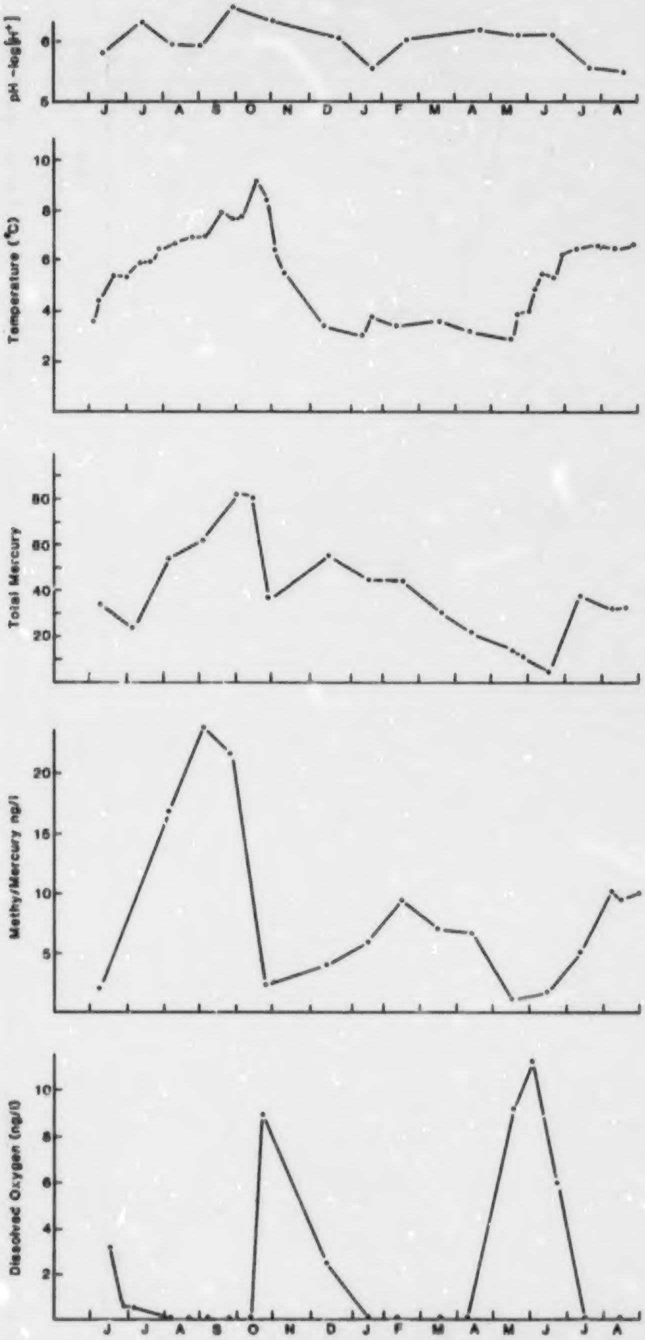


Figure 4.20 Selected water quality parameters for Clay Lake, western basin (site 9), 1m above bottom (18m), June 1978 to August 1979.

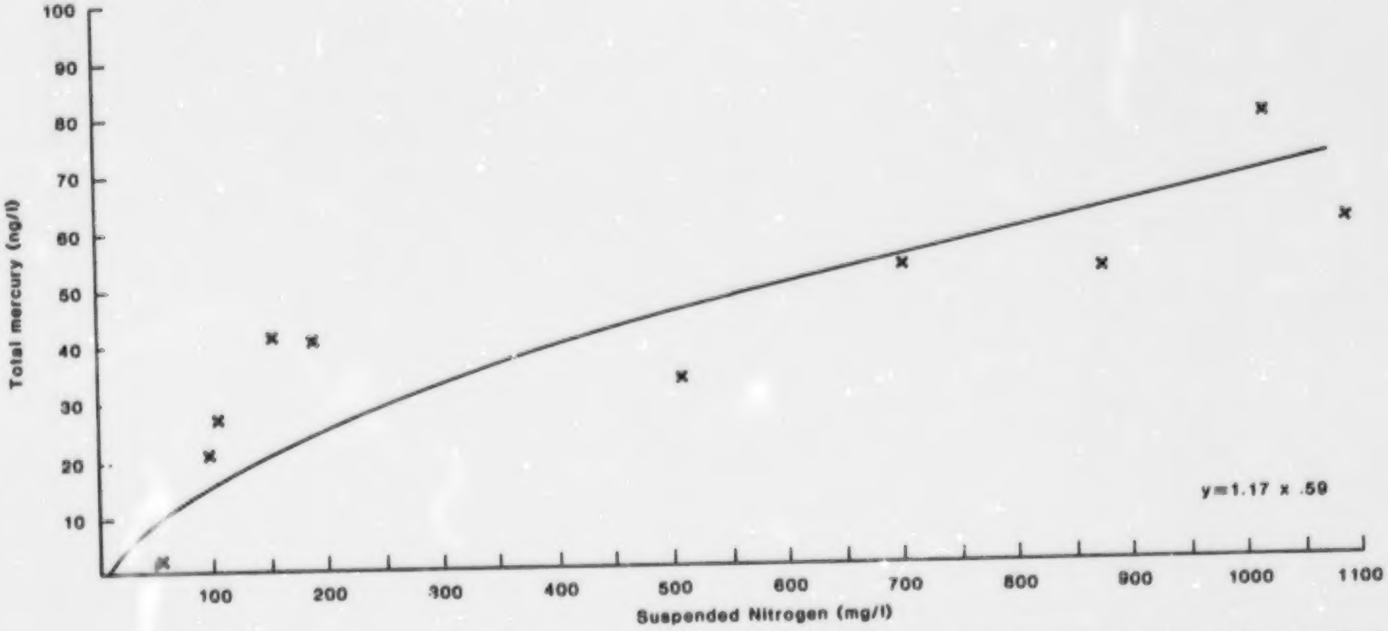


Figure 4.21 Relationship between Total mercury concentrations and suspended nitrogen levels Clay Lake -western basin (Site 9) 1m above bottom, August, 1975 July, 1979.

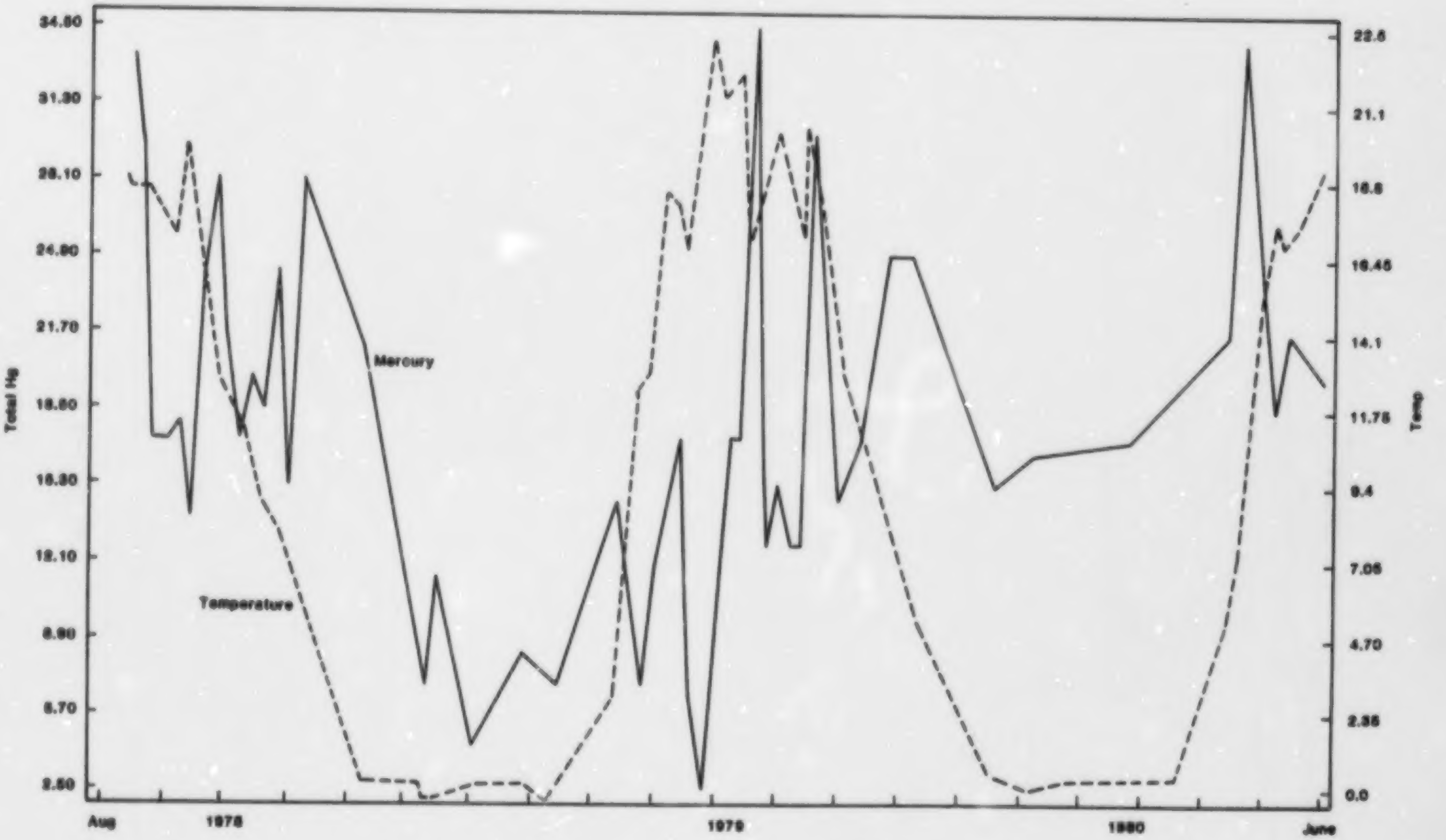


Figure 4.22 Mercury concentration and temperature Clay Lake outflow (site 10), August, 1978–June, 1980.

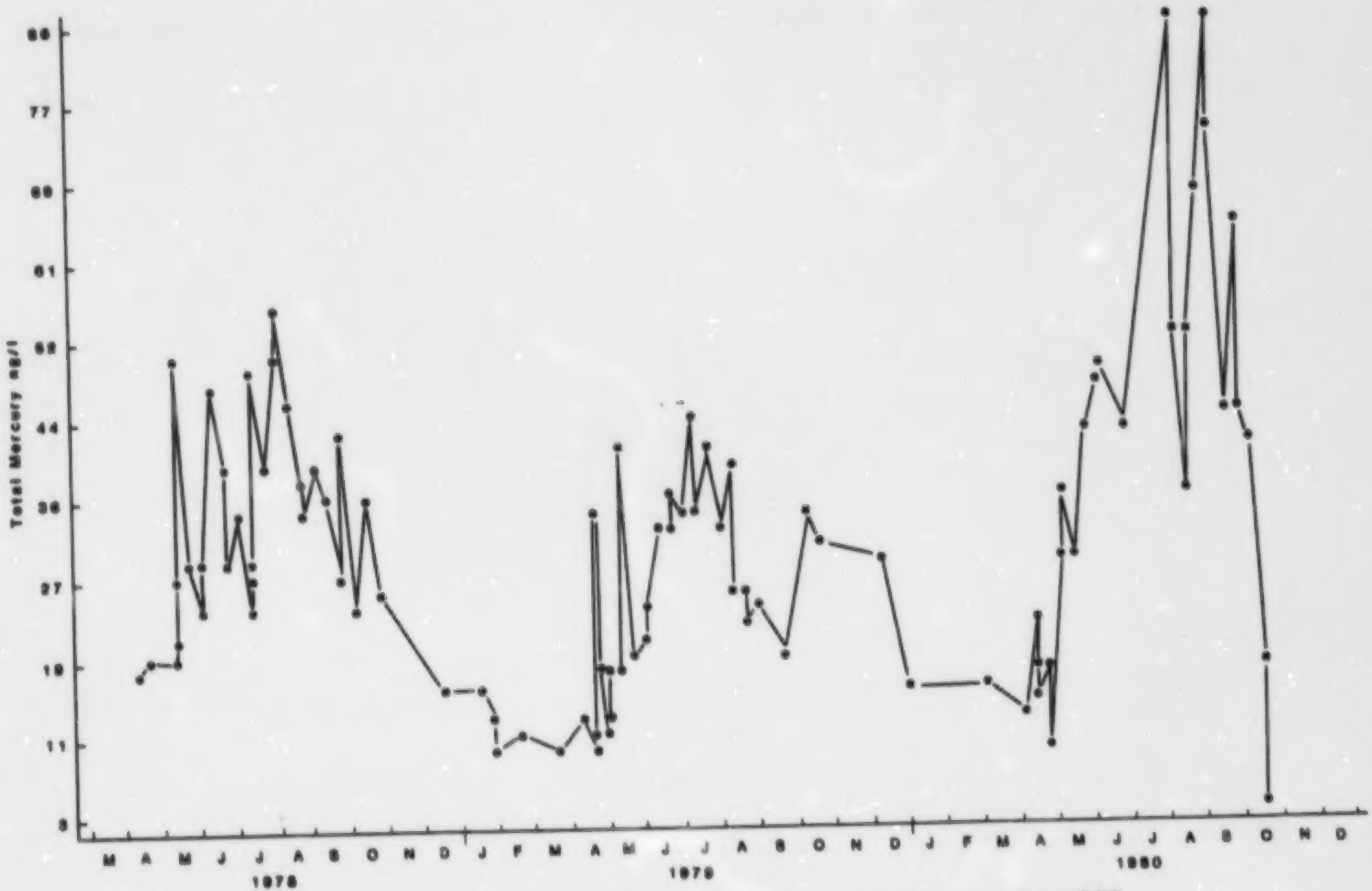


Figure 4.23 Mercury concentrations, Clay Lake inflow (site 7), March 1978 to December 1980.

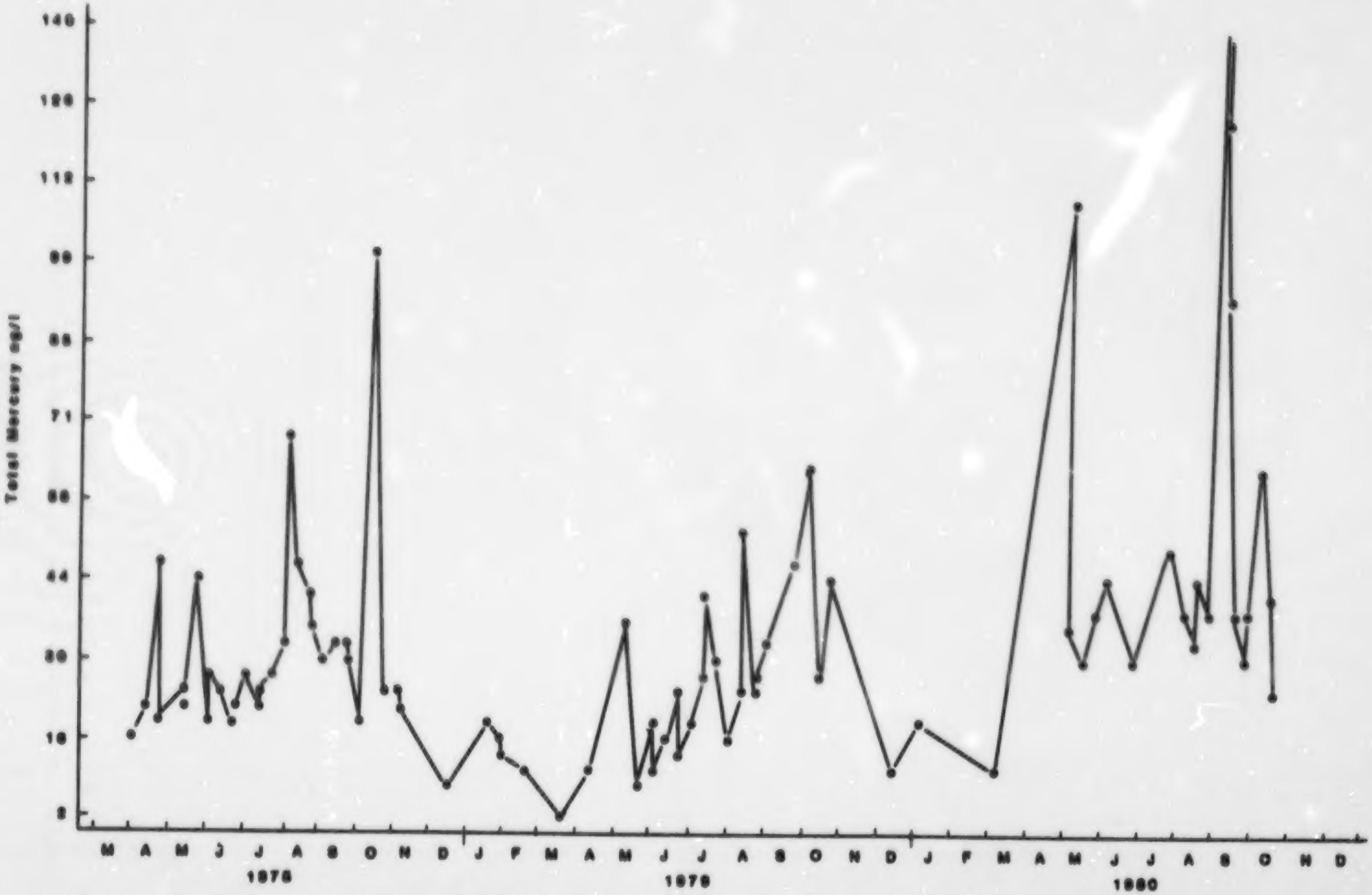


Figure 4.24 Mercury concentrations Clay Lake, eastern basin (site 8), March 1978 to December 1980.

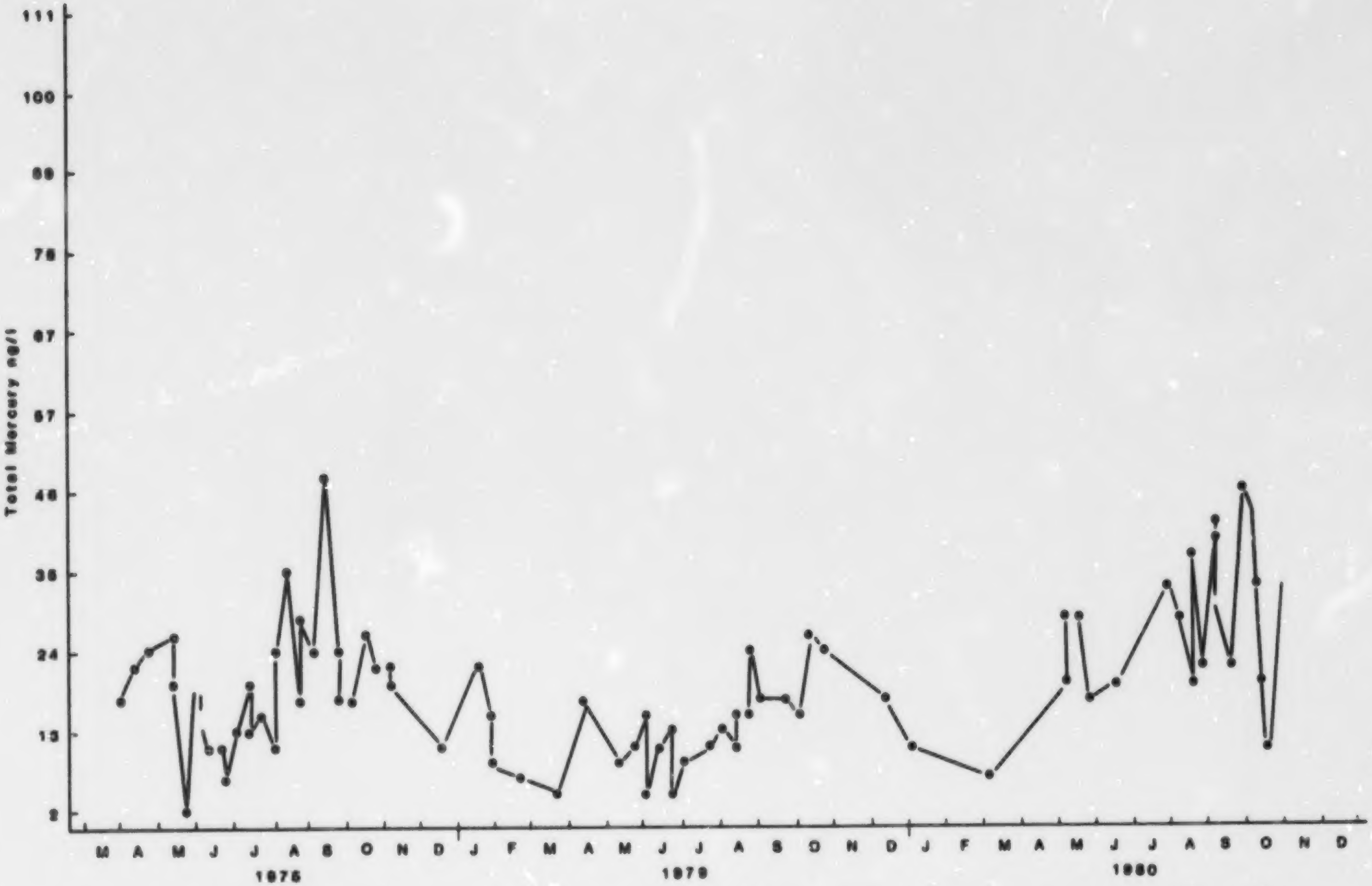


Figure 4.25 Mercury concentrations Clay Lake, western epilimnion (site 9), March 1978 to December 1980.

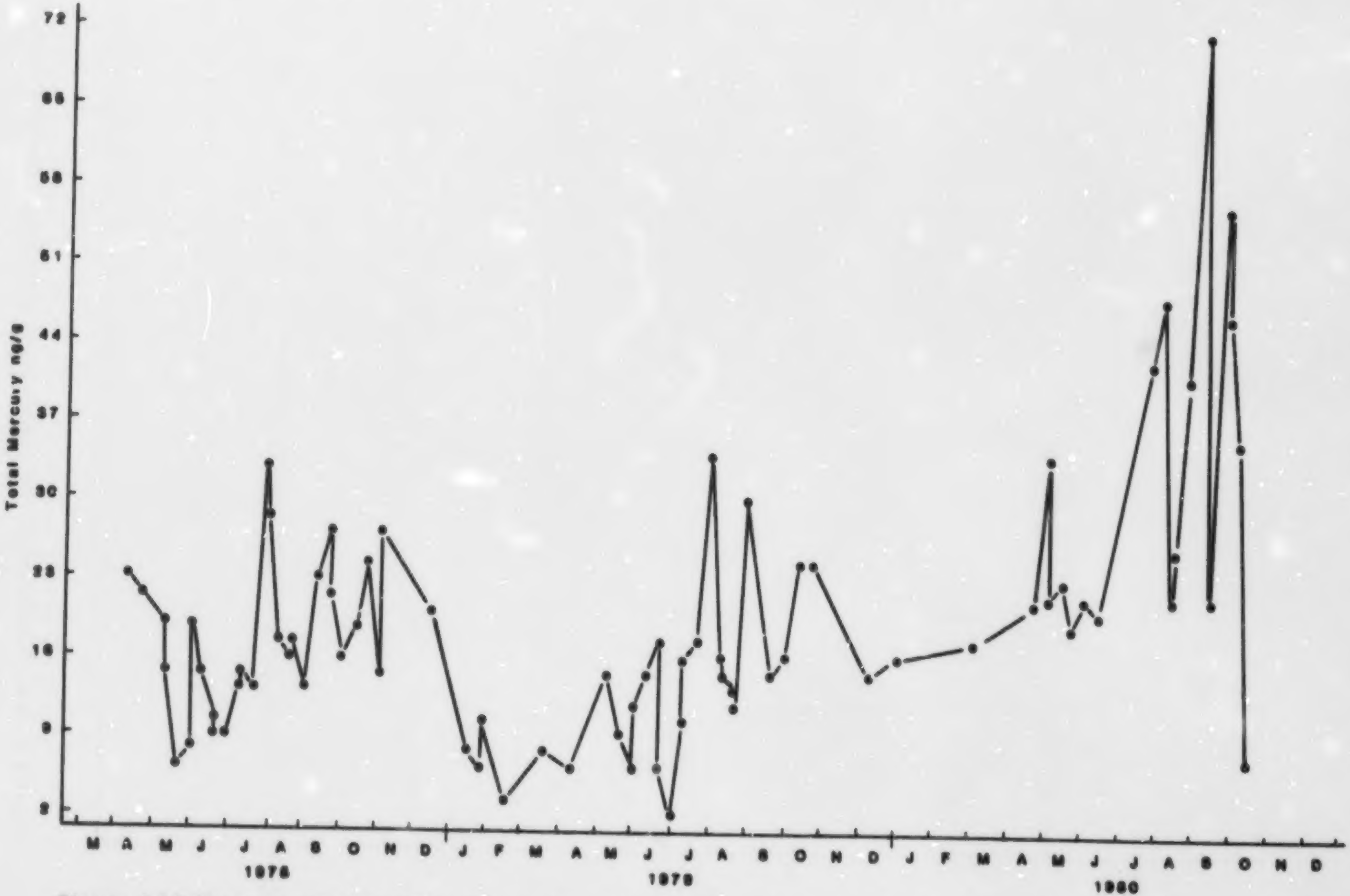


Figure 4.26 Mercury concentrations Clay Lake, outflow (site 10), March 1978 to December 1980.

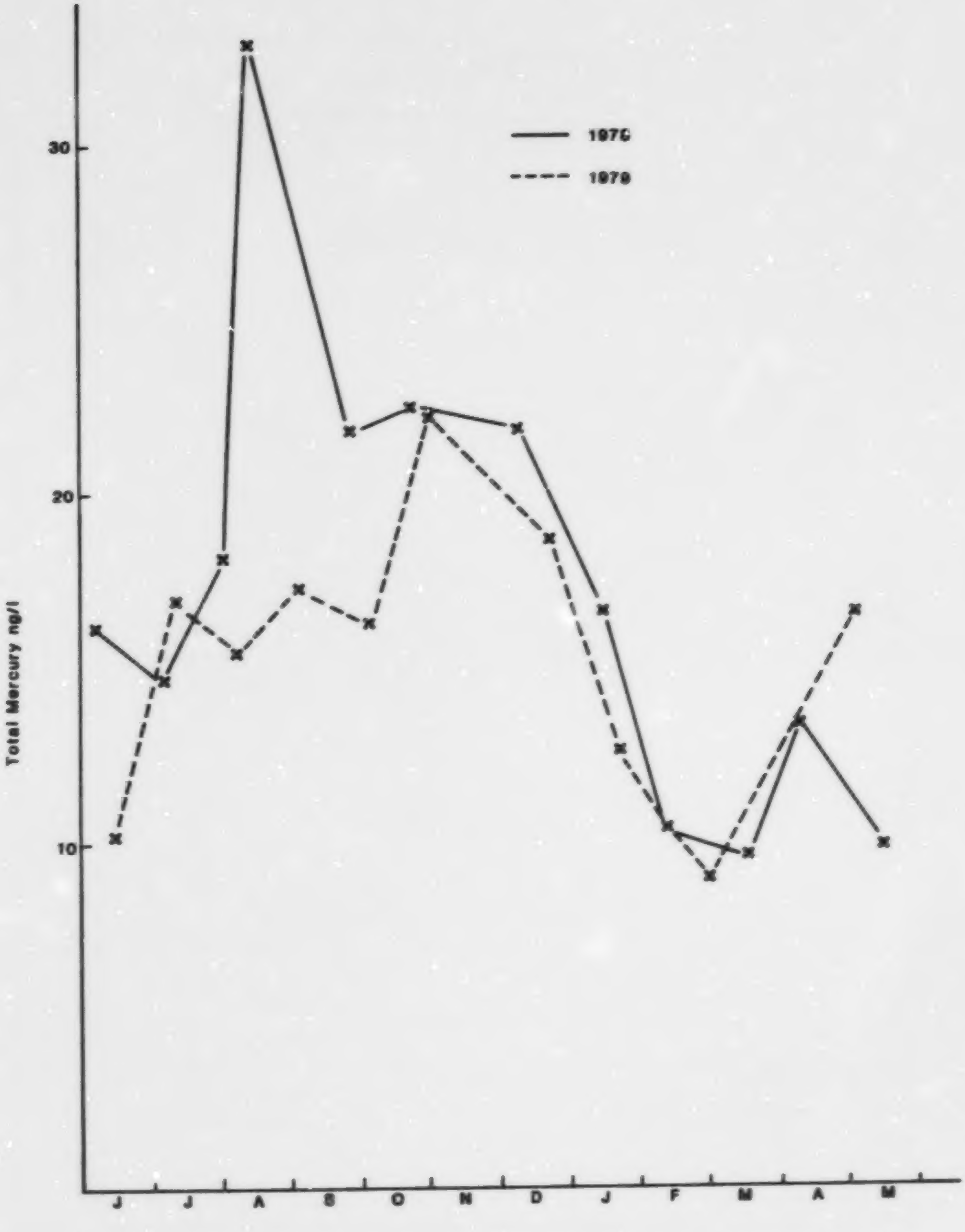


Figure 4.27 Mean monthly whole lake mercury concentrations, Clay Lake, June 1978–June 1980.

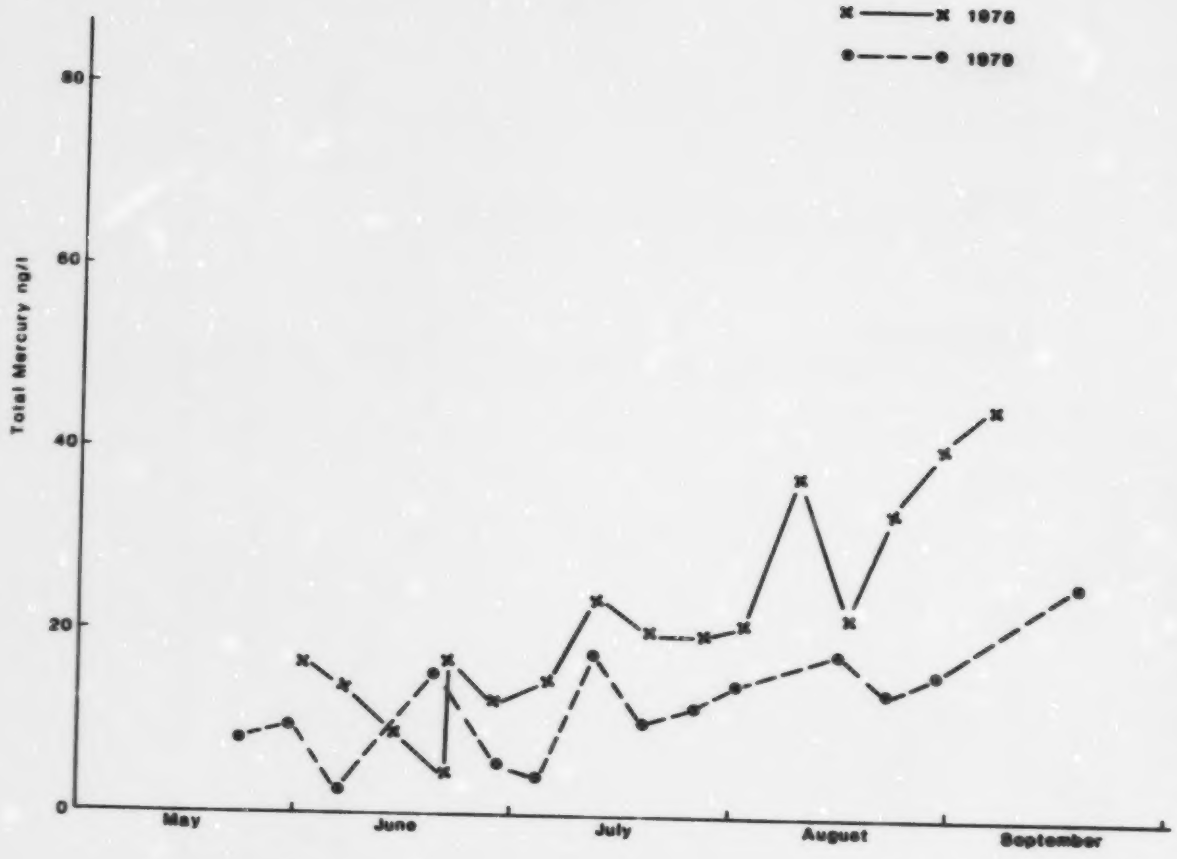


Figure 4.28 Mercury concentrations, Clay Lake metalimnion , 1978 and 1979.

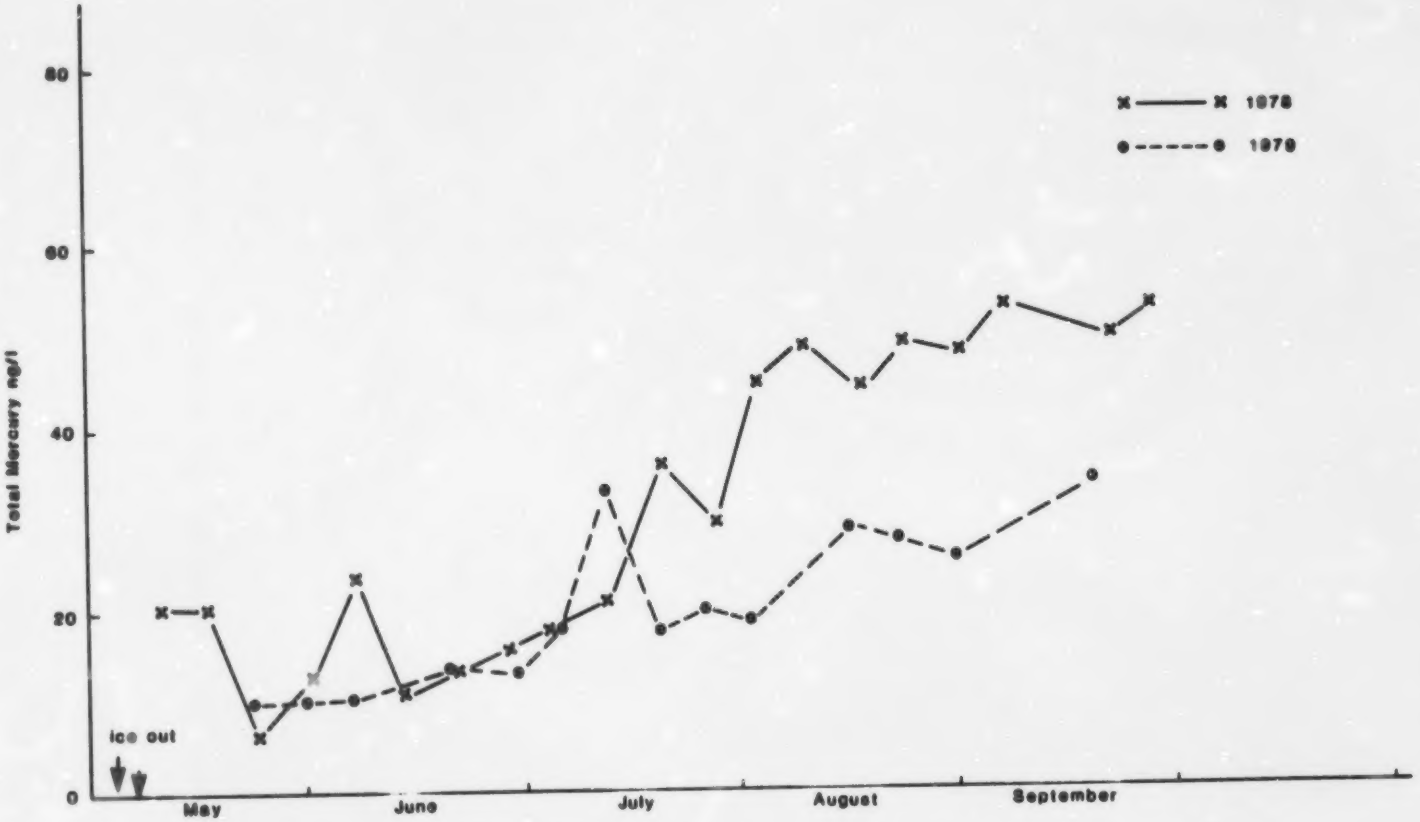


Figure 4.29 Mercury concentrations, Clay Lake hypolimnio, 1978 and 1979.

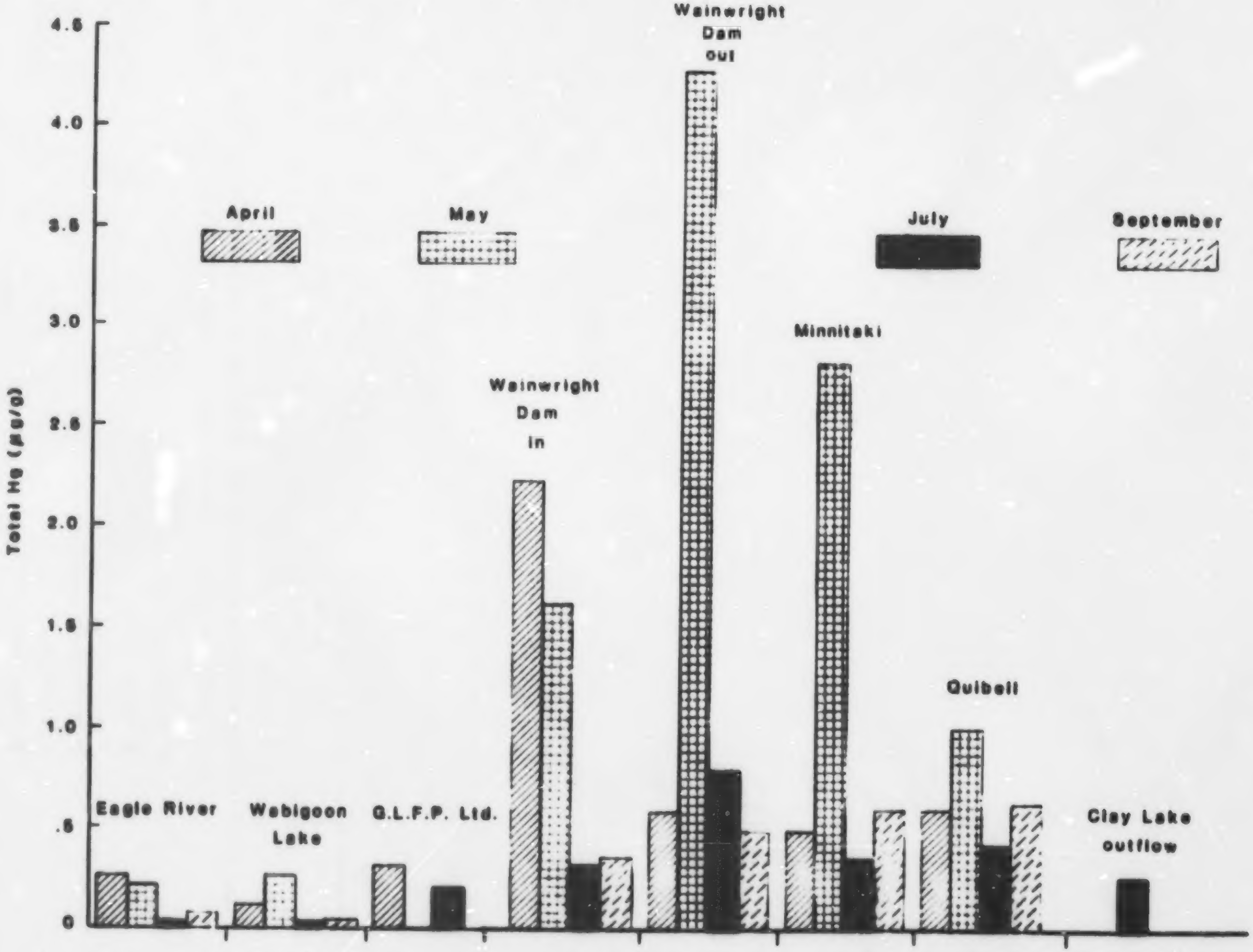


Figure 4.30 Total mercury concentrations in suspended sediments in the Wabigoon River system, 1979.

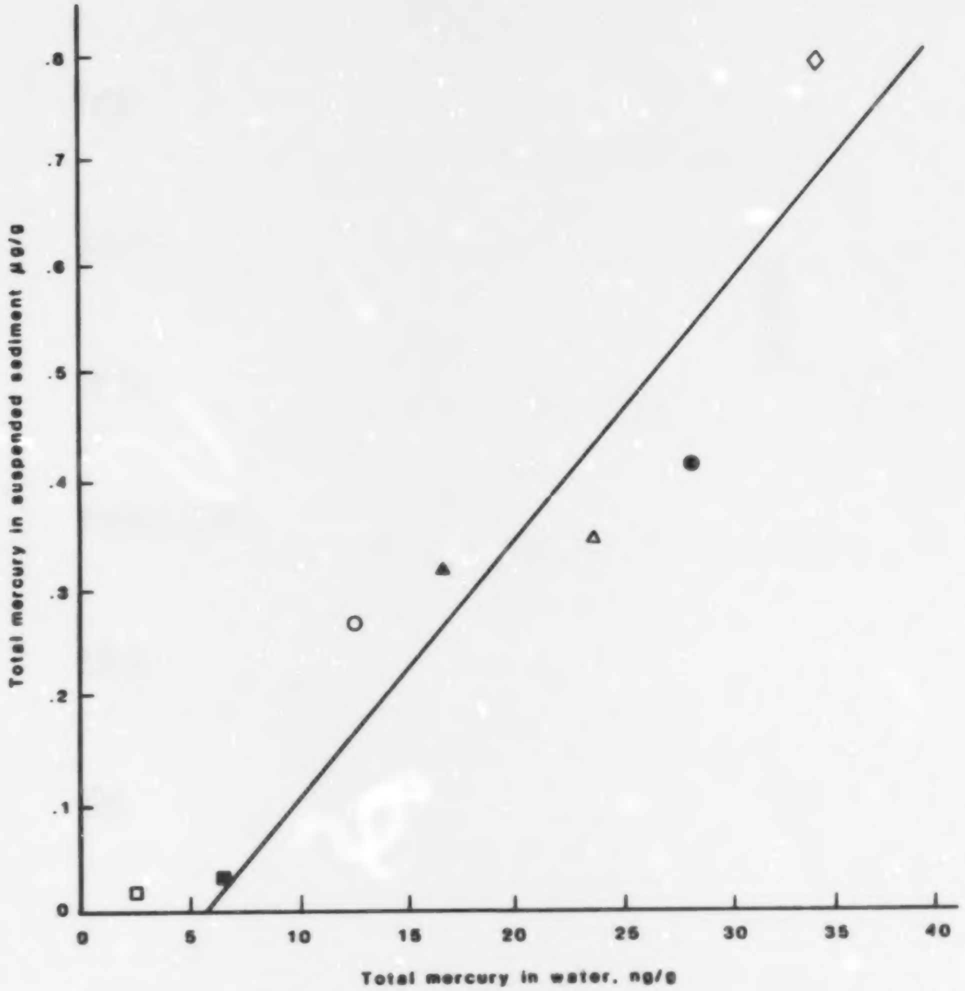


Figure 4.31 Relationship between total mercury in suspended sediment and total mercury in water, July, 1979. r=.93 p<.01

□ Wabigoon Lake
■ Eagle River
△ Wainwright Dam inflow
◇ Wainwright Dam outflow
▲ Minnitaki
● Clay Lake outflow

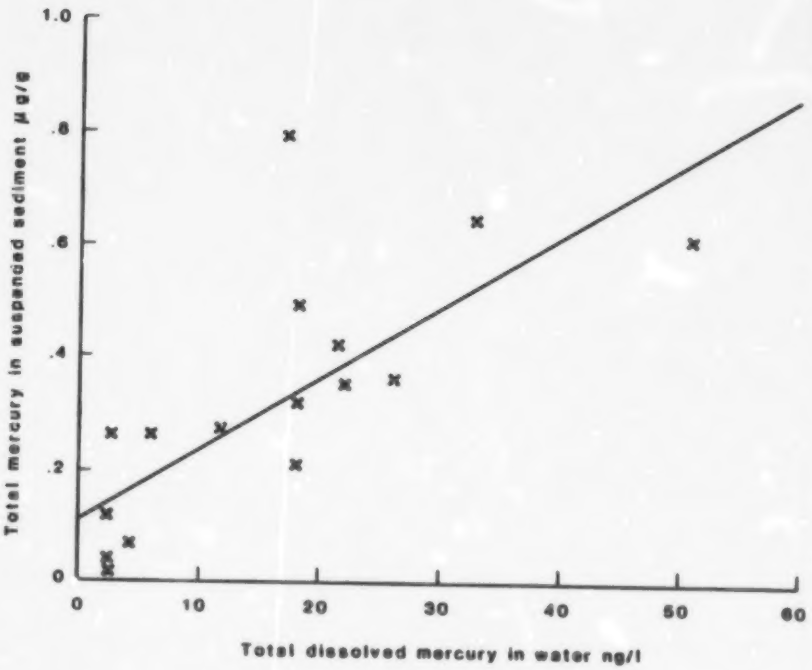


Figure 4.32 Relationship between dissolved and suspended total mercury concentrations in the Wabigoon River system during non-high flow conditions. n=17, r=.71, p<.01

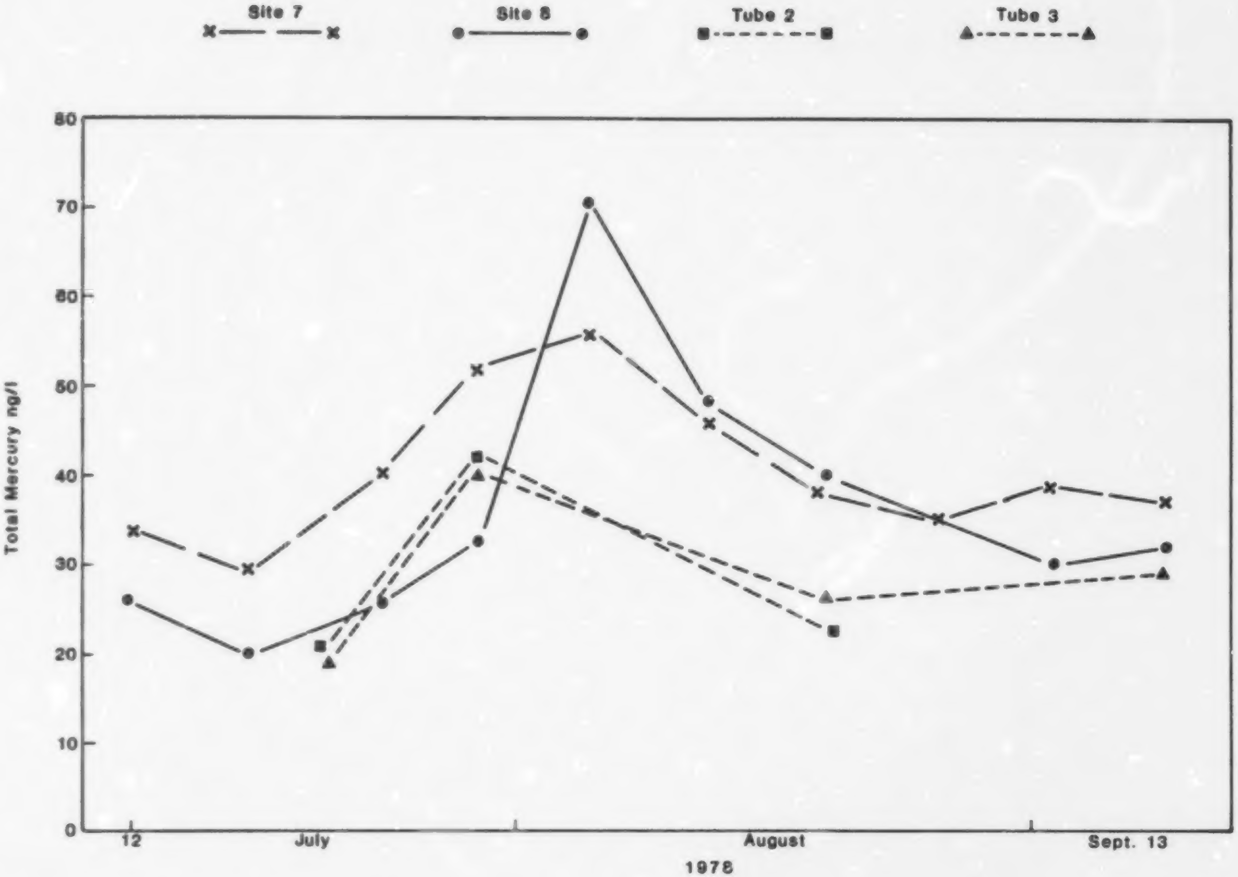


Figure 4.33 Mercury trends in water at four sites.

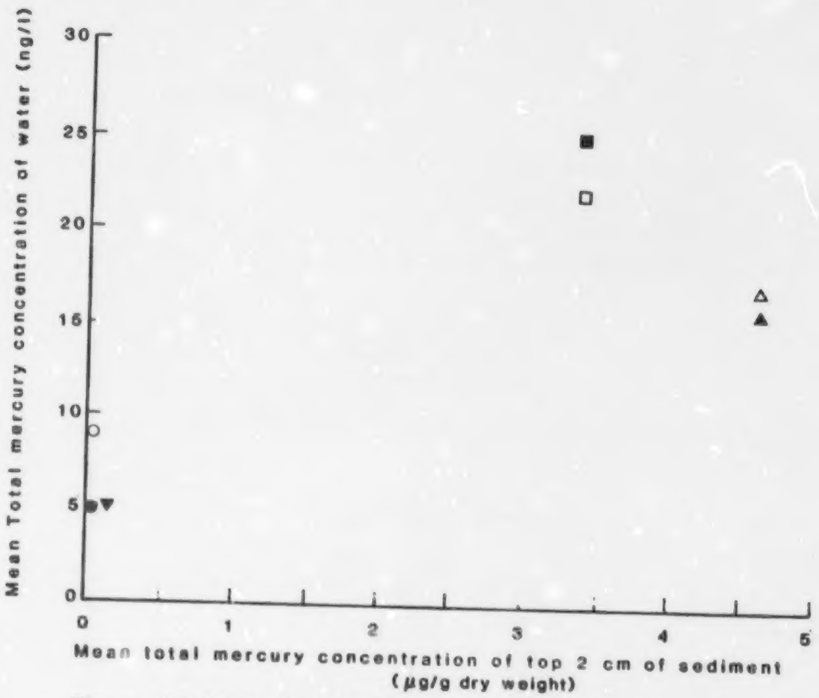


Figure 4.34 Relationship between mercury in water and sediment at selected sites in the Wabigoon/English River system for 2 consecutive study periods of 12 months

Open symbols: first study year
Closed symbols: second study year
○ ● Wabigoon Lake
□ ■ Clay Lake Eastern Basin
△ ▲ Clay Lake Western Basin
▼ English River upstream of Ball Lake (sediment from Maynard Lake)

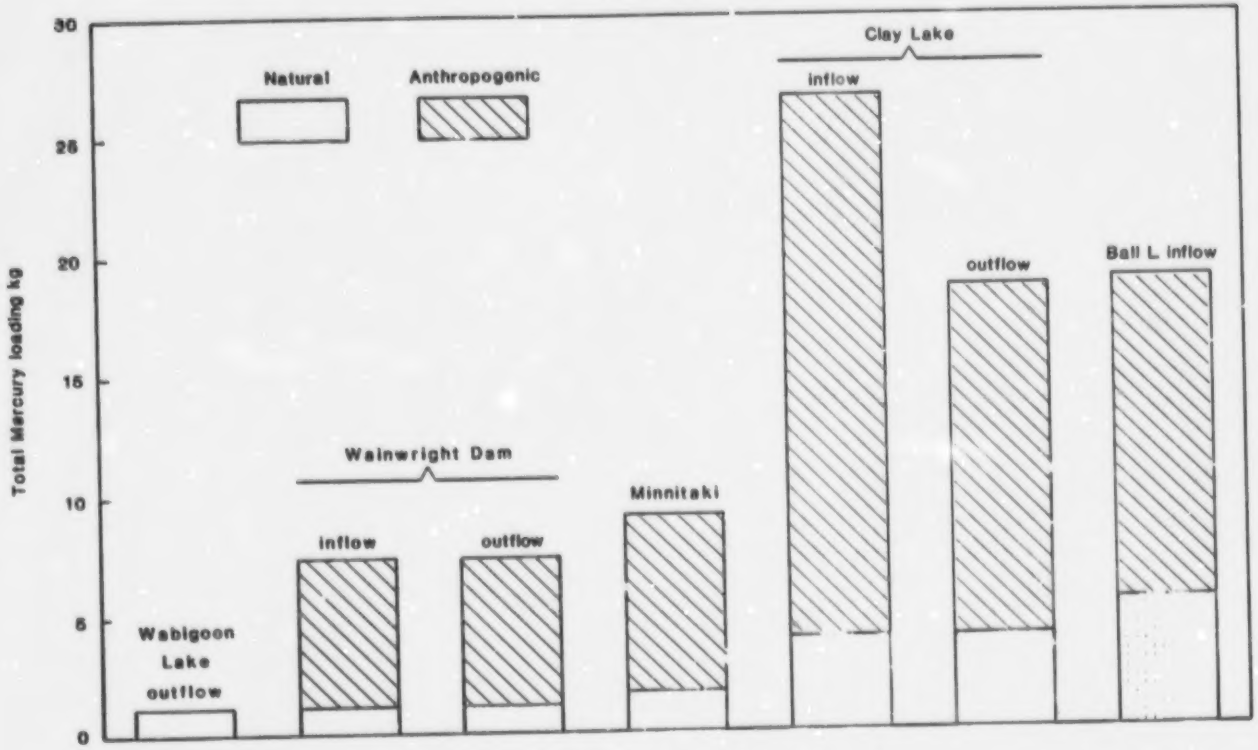


Figure 4.35 Mercury loadings in the Wabigoon River system July 1979–June 1980

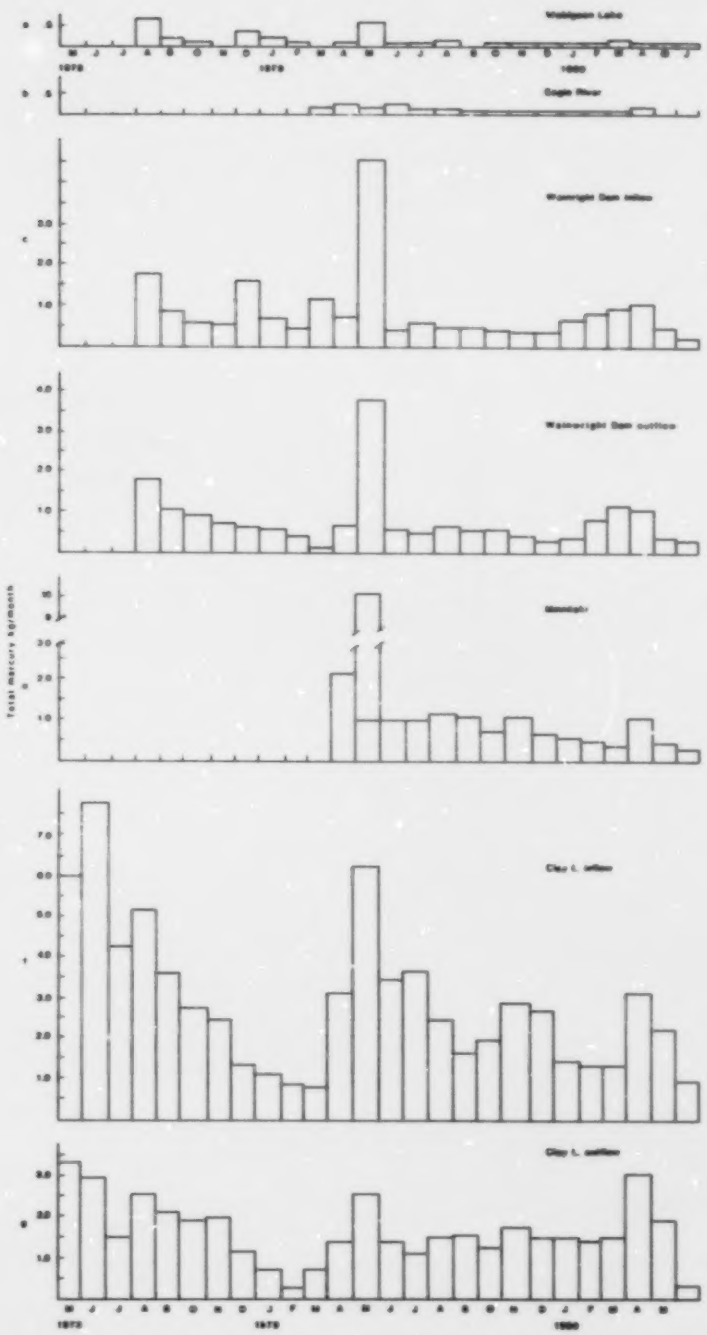


Figure 4.36 Monthly mercury loadings for selected sites on the Wabigoon River system, May, 1978–June 1980.

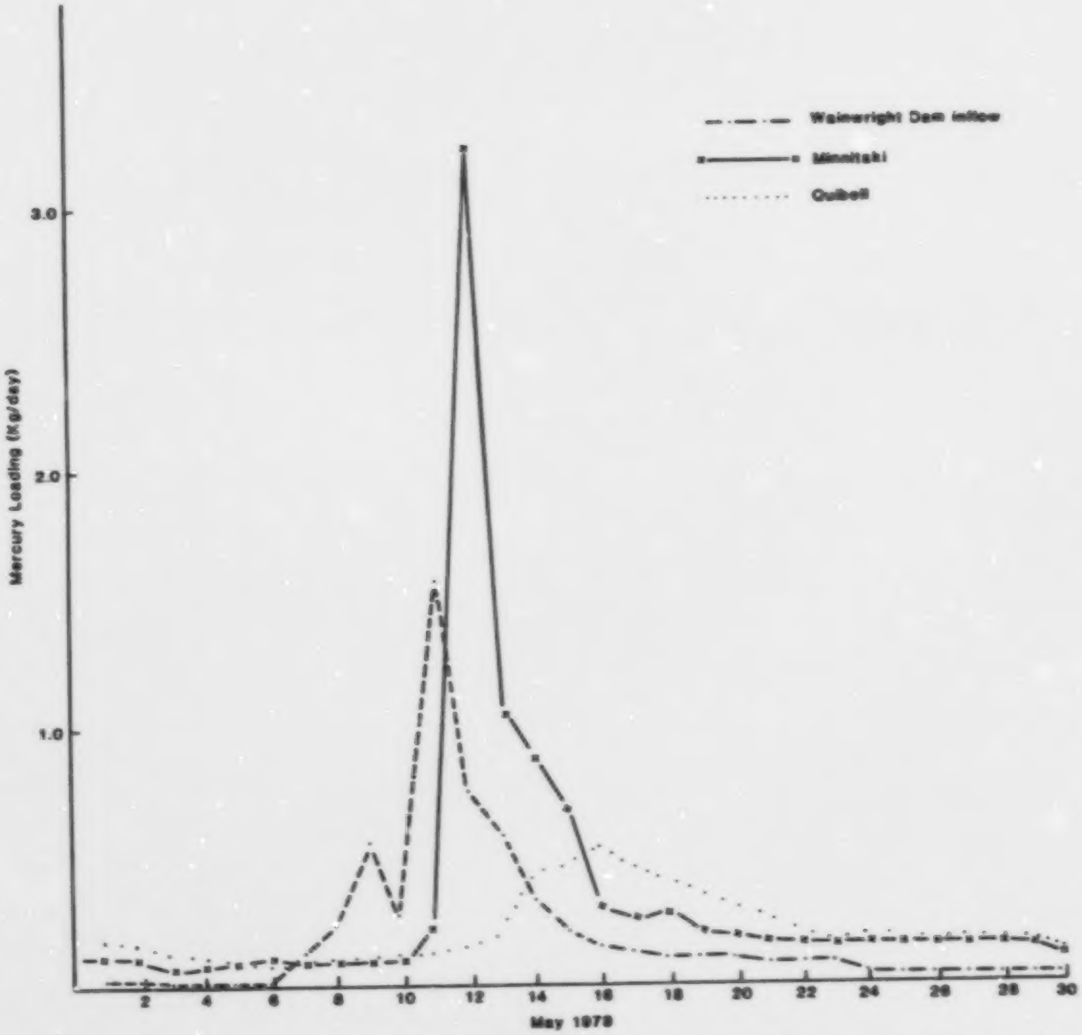


Figure 4.37 Daily mercury loadings at selected sites in the Wabigoon River during the controlled flood discharge at Dryden, May 1979.

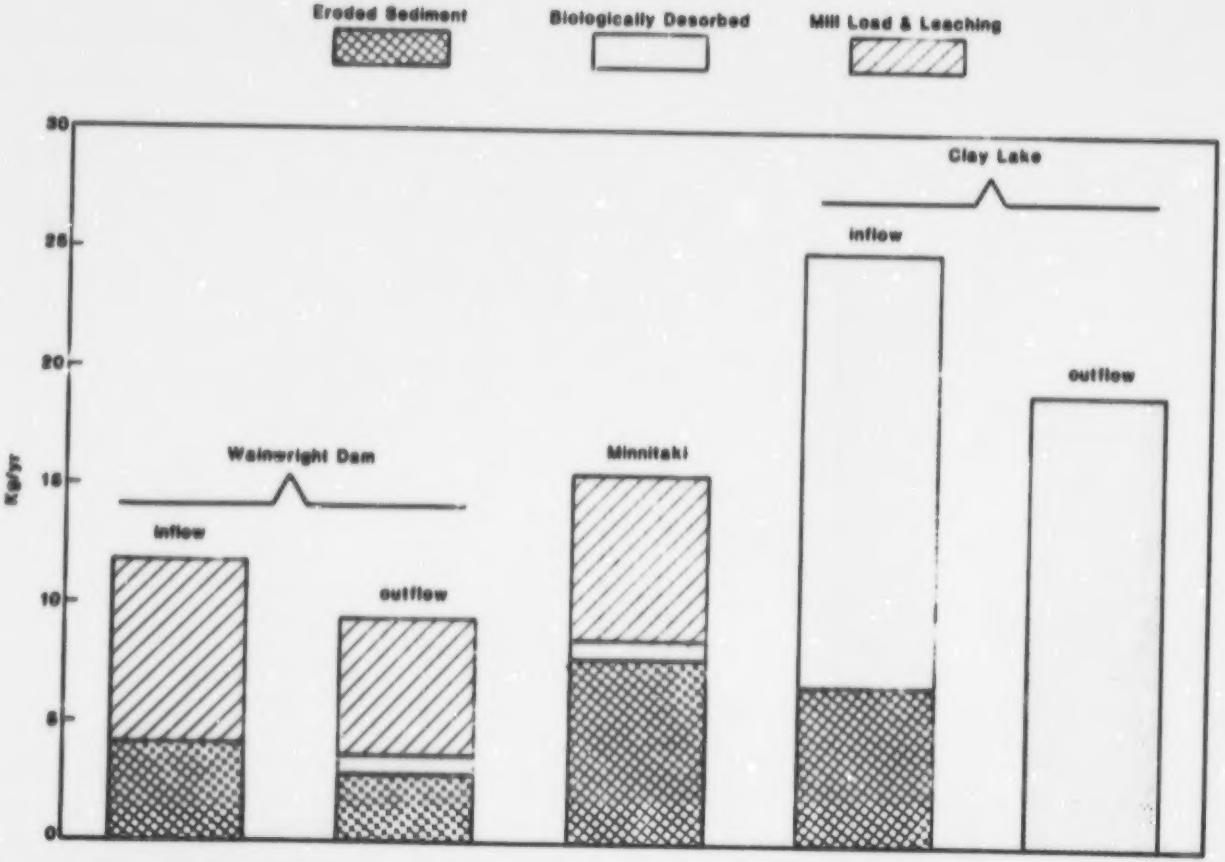


Figure 4.38 Annual anthropogenic mercury sources in the Wabigoon River system for a typical hydrological year.

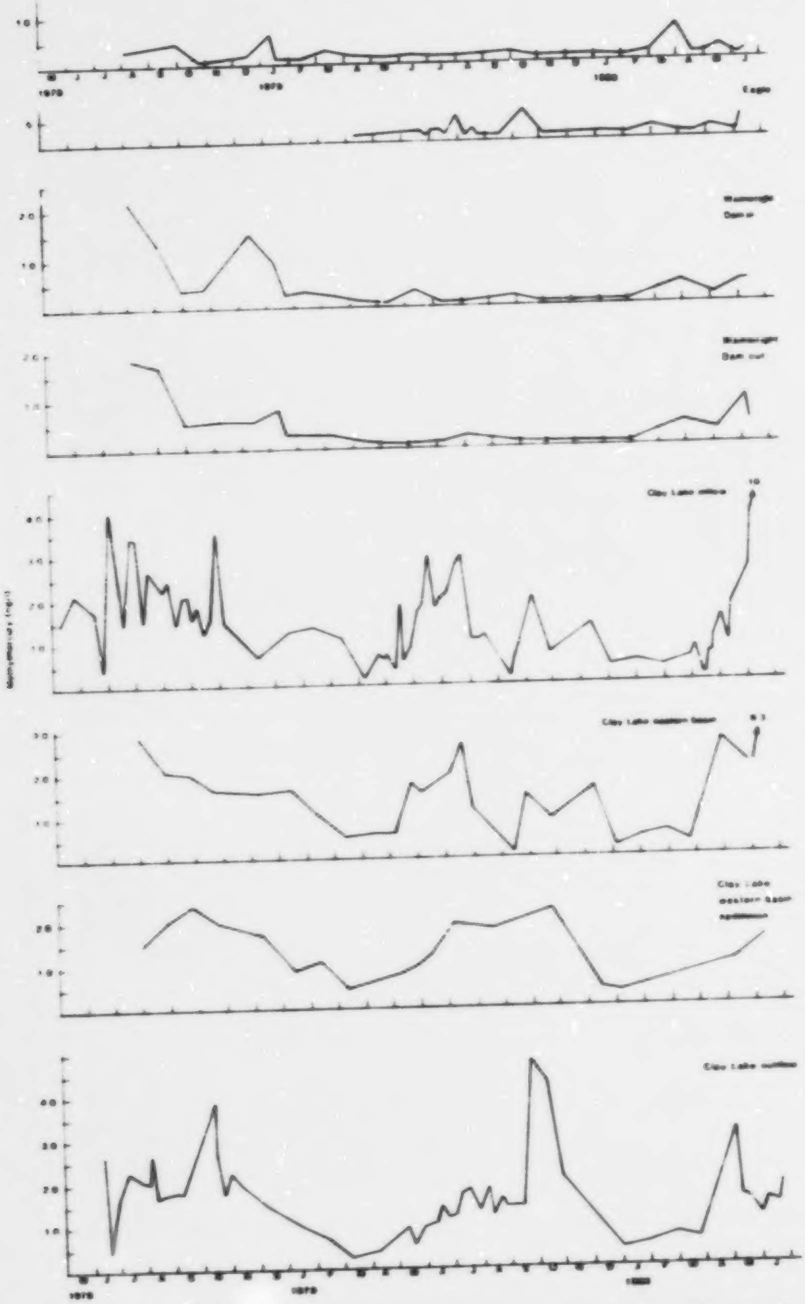


Figure 4.39 Methylmercury concentrations for selected sites in the Wabigoon River system, May, 1978–June, 1980.

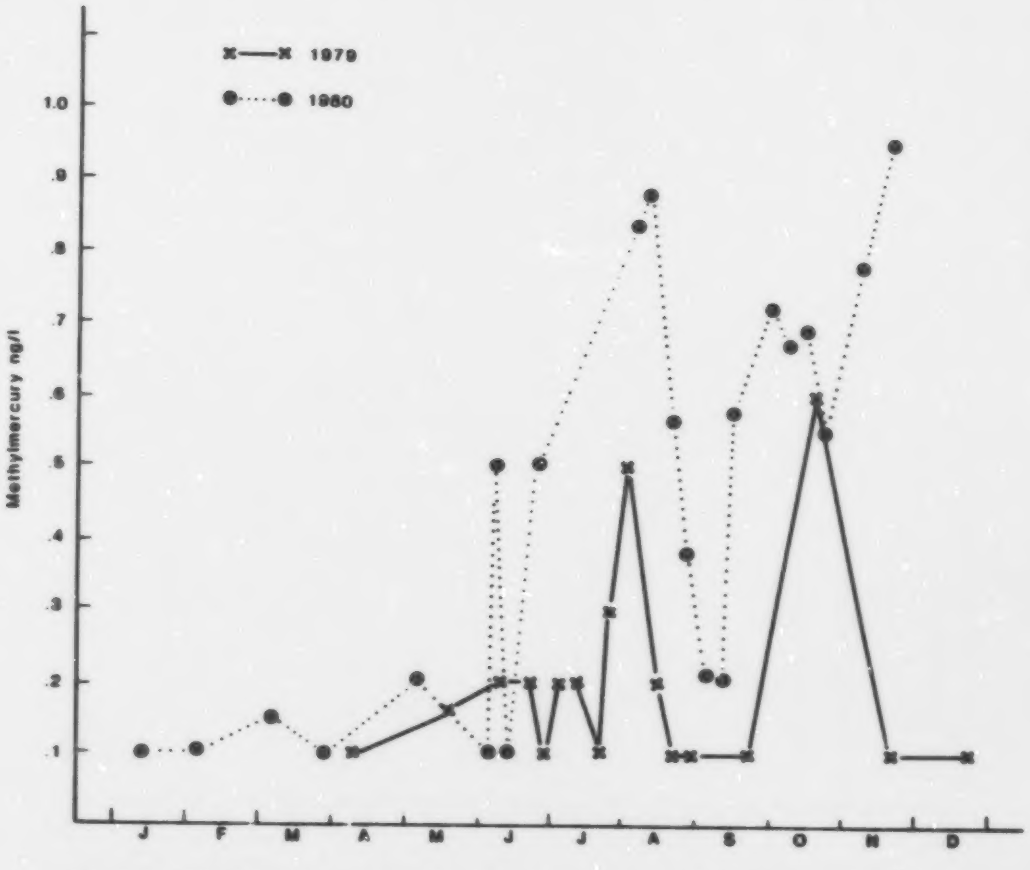


Figure 4.40 Methylmercury concentrations, Eagle River, April 1979–Nov 1980

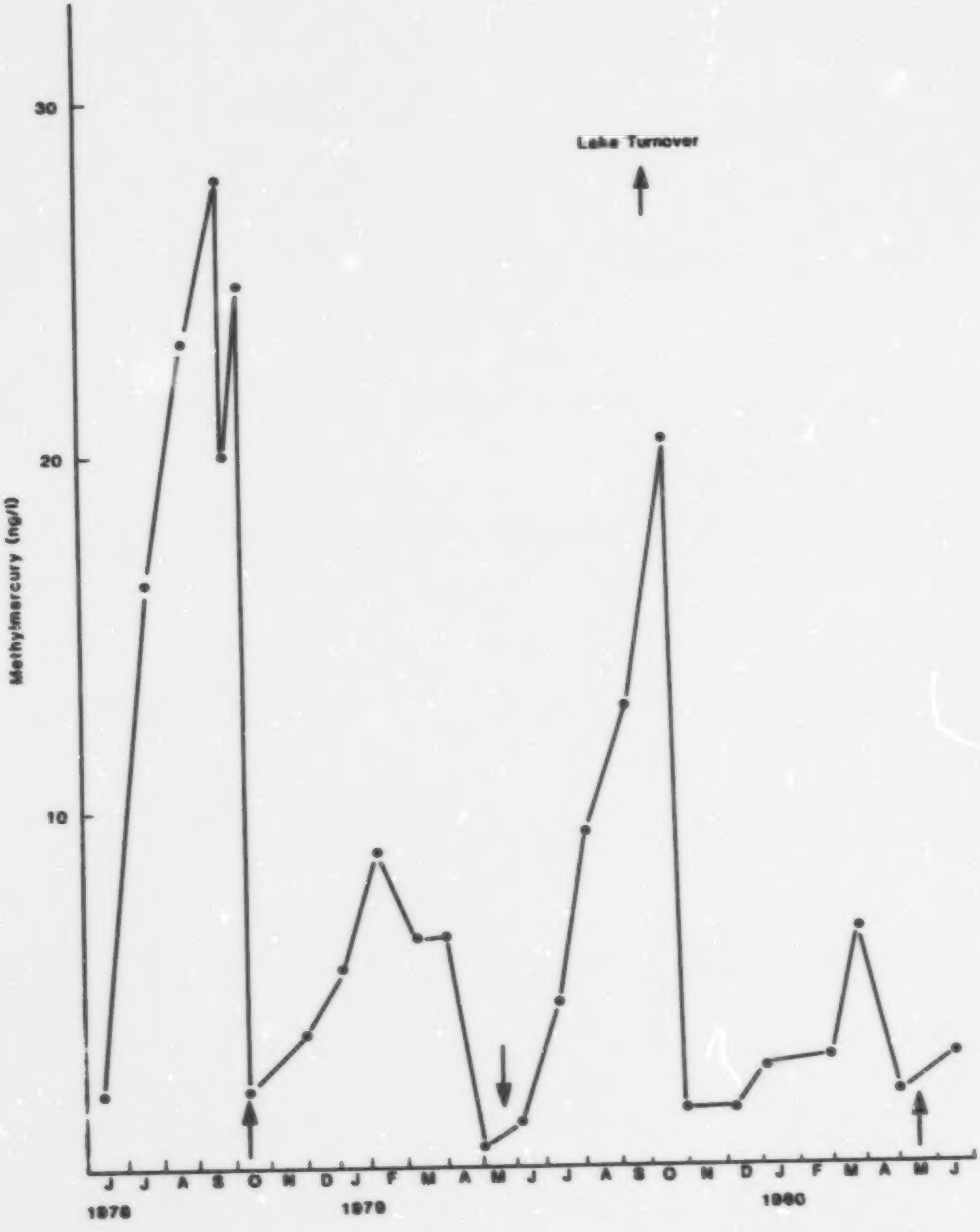


Figure 4.41 Methylmercury concentrations, Clay Lake–western basin (site 9) 1m above bottom, June 1978–June, 1980.

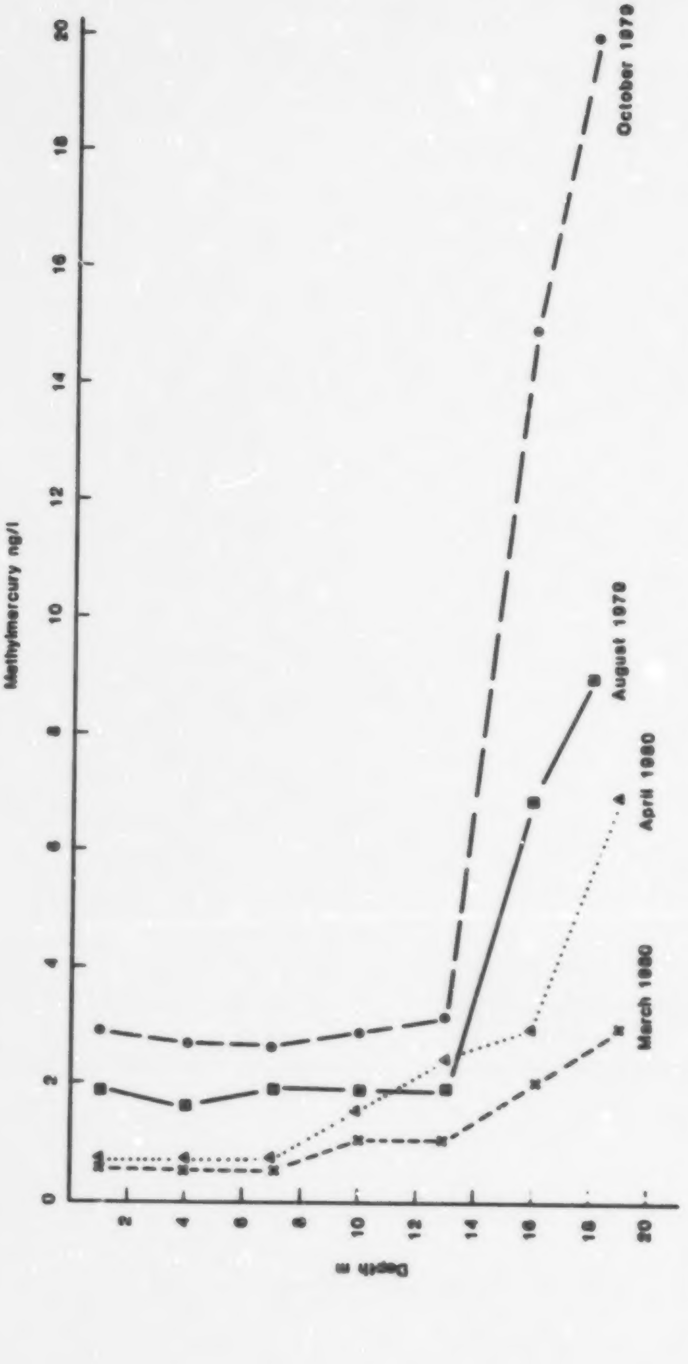


Figure 4.42 Methylmercury profiles, Clay Lake western basin (Site 9)

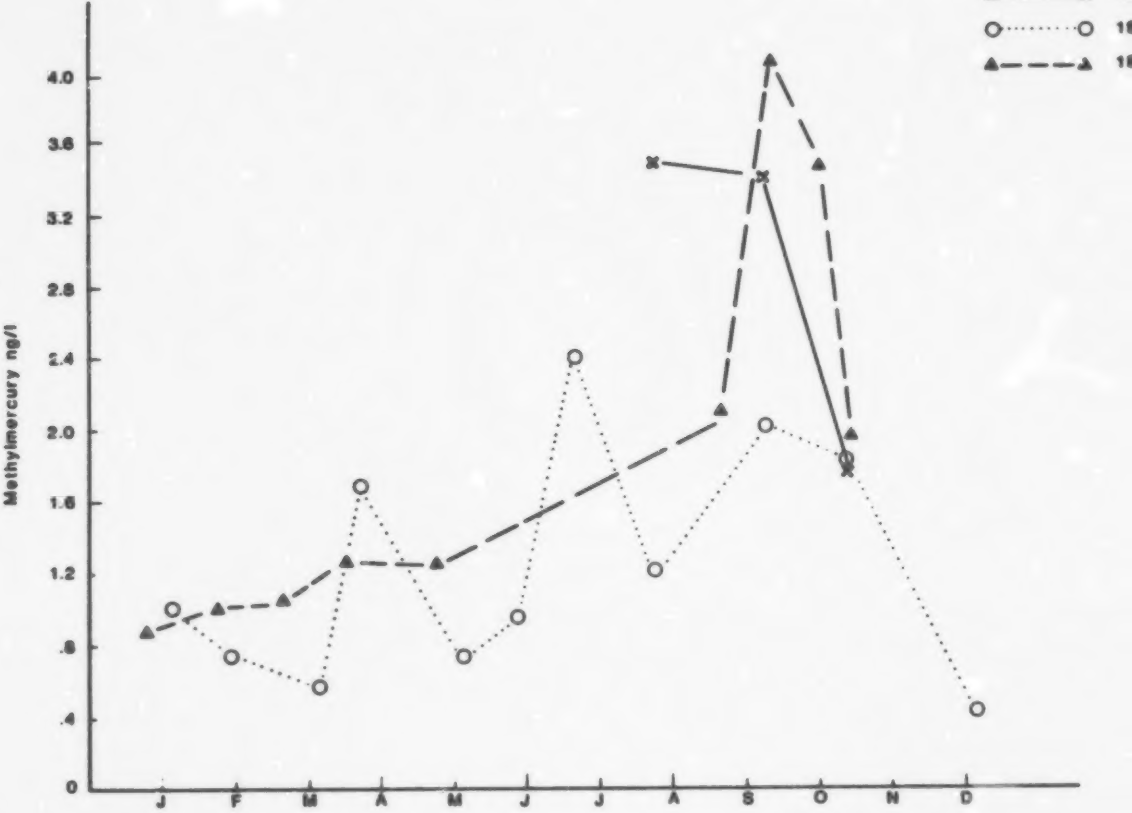


Figure 4.43 Mean whole lake Methylmercury concentrations, Clay Lake Aug 1978-Nov 1980

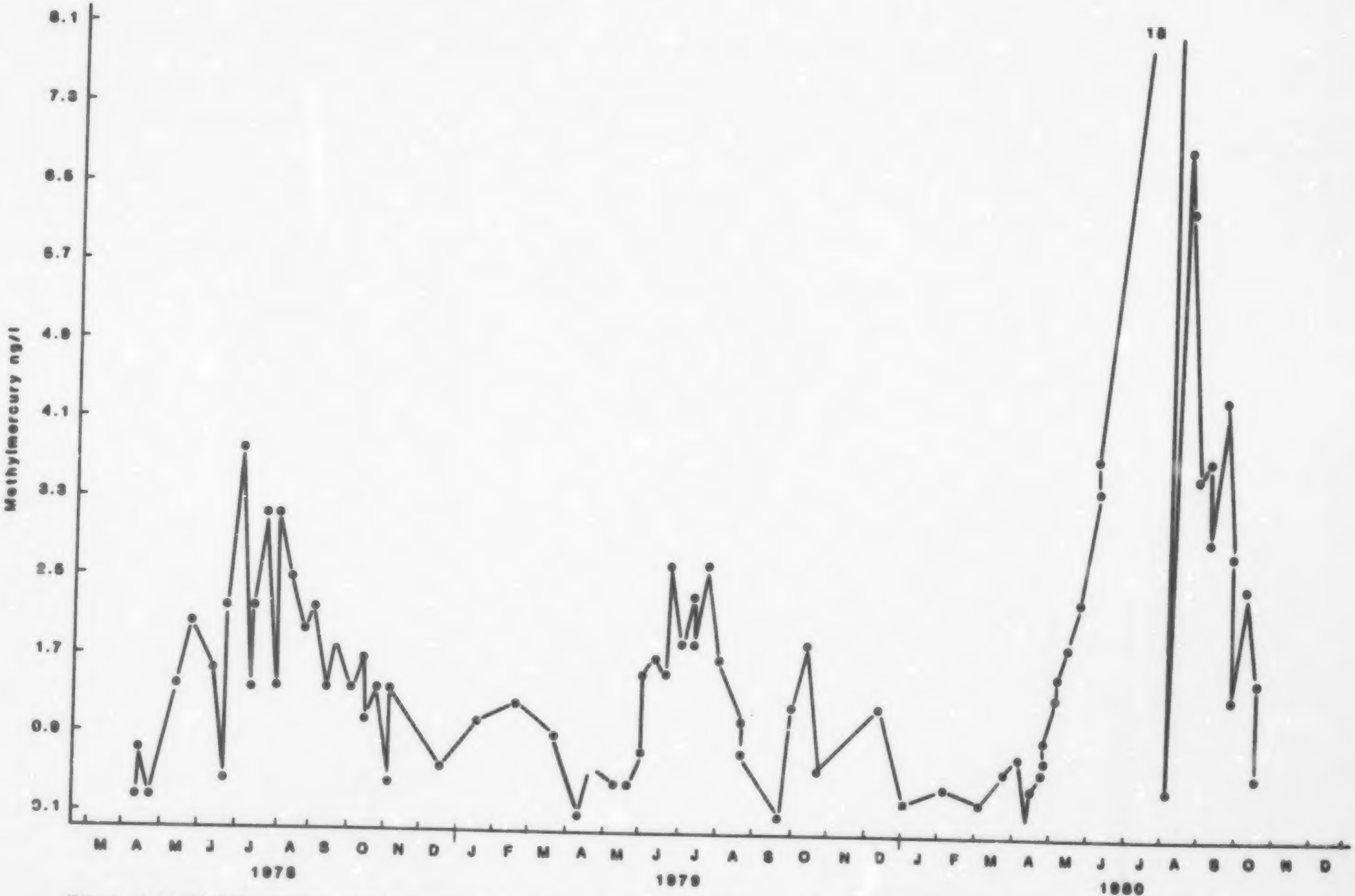


Figure 4.44 Methylmercury concentrations, Wabigoon River inflow to Clay Lake, site 7, March, 1978–November, 1980.

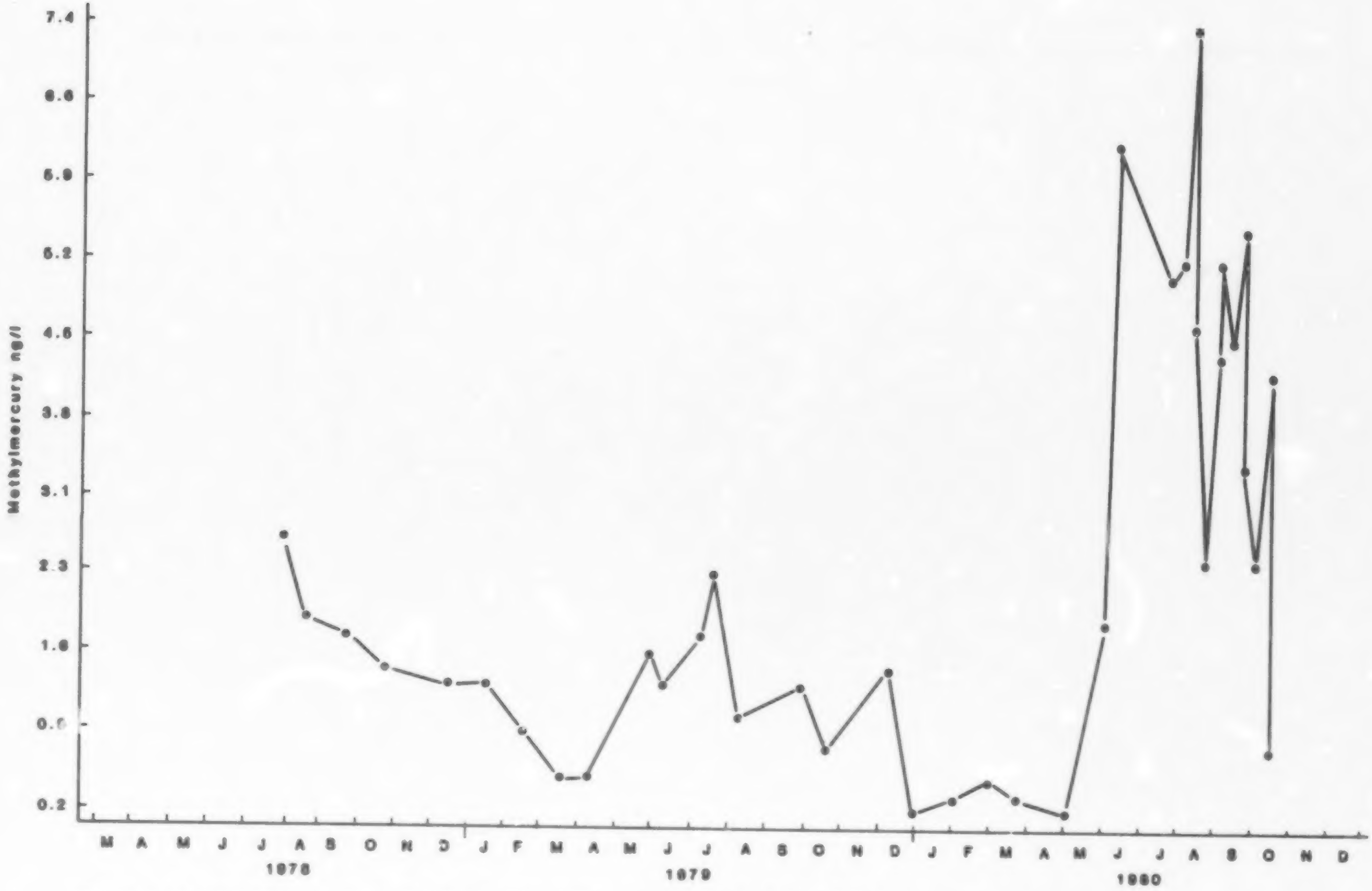


Figure 4.45 Methylmercury concentrations, Clay Lake, eastern basin (site 8), August, 1978–November, 1980.

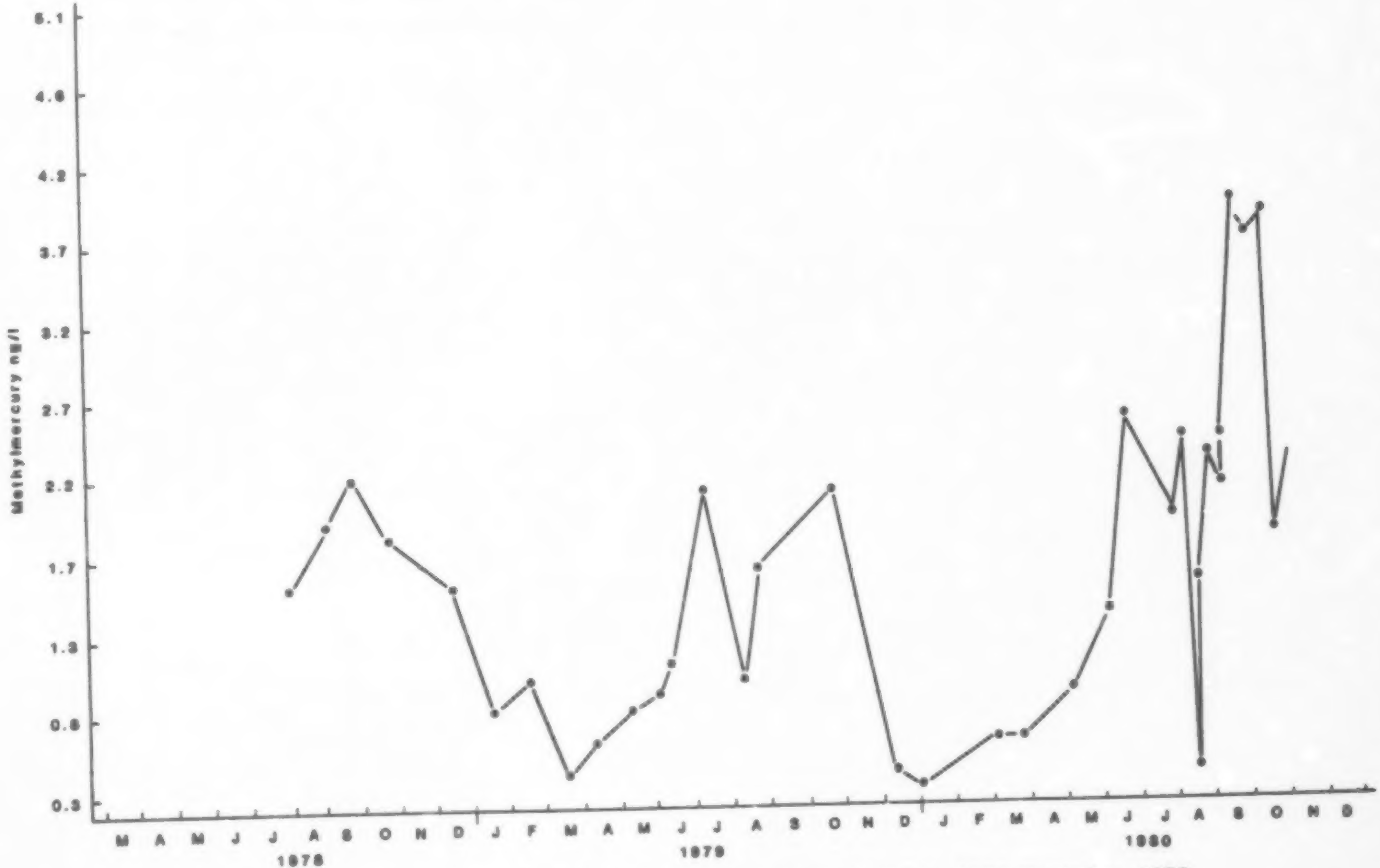


Figure 4.46 Methylmercury concentrations, Clay Lake western basin (site 9), August, 1978–November, 1980.

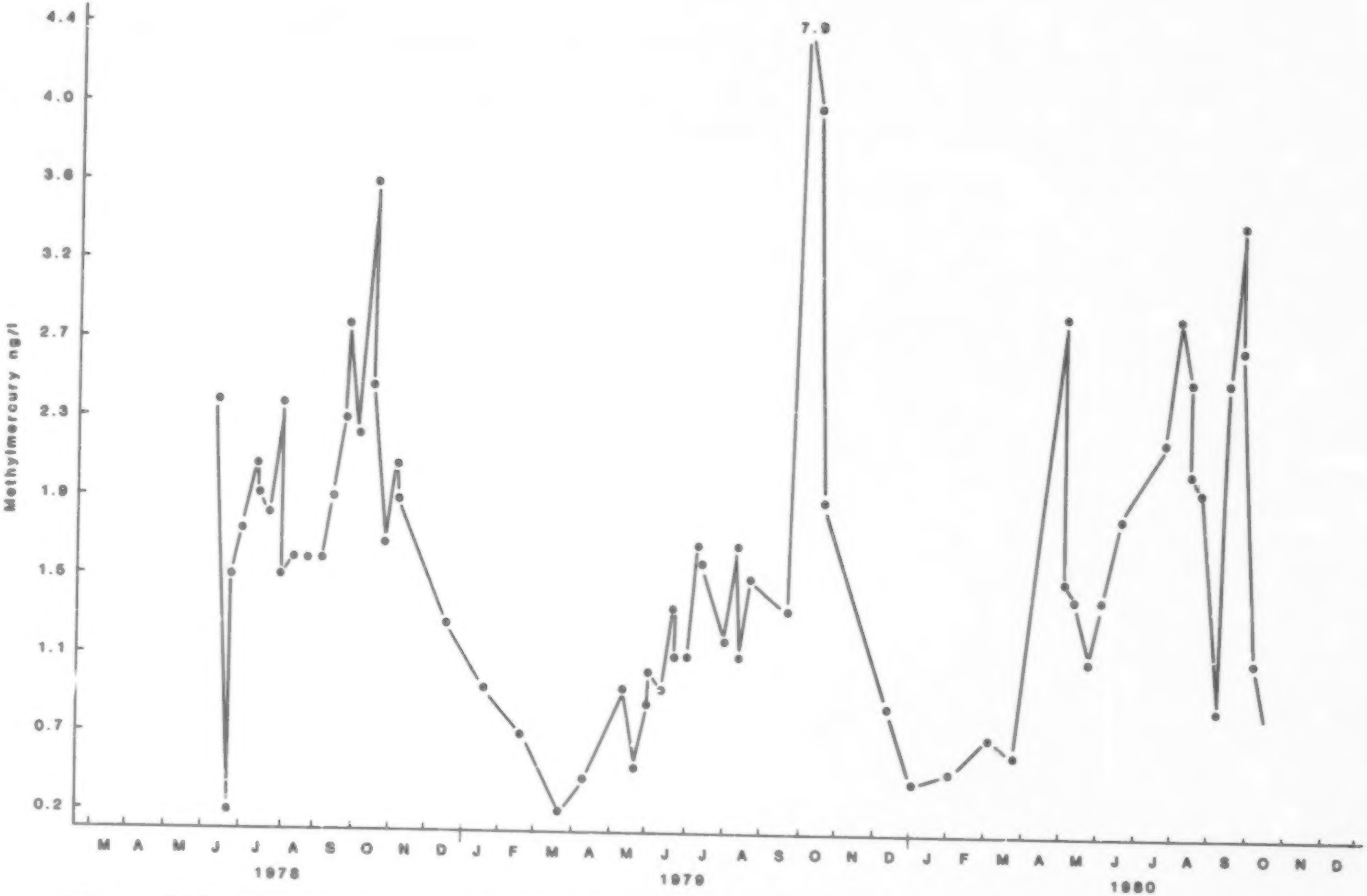


Figure 4.47 Methylmercury concentrations, Clay Lake outflow (site 10), May, 1978–November, 1980.

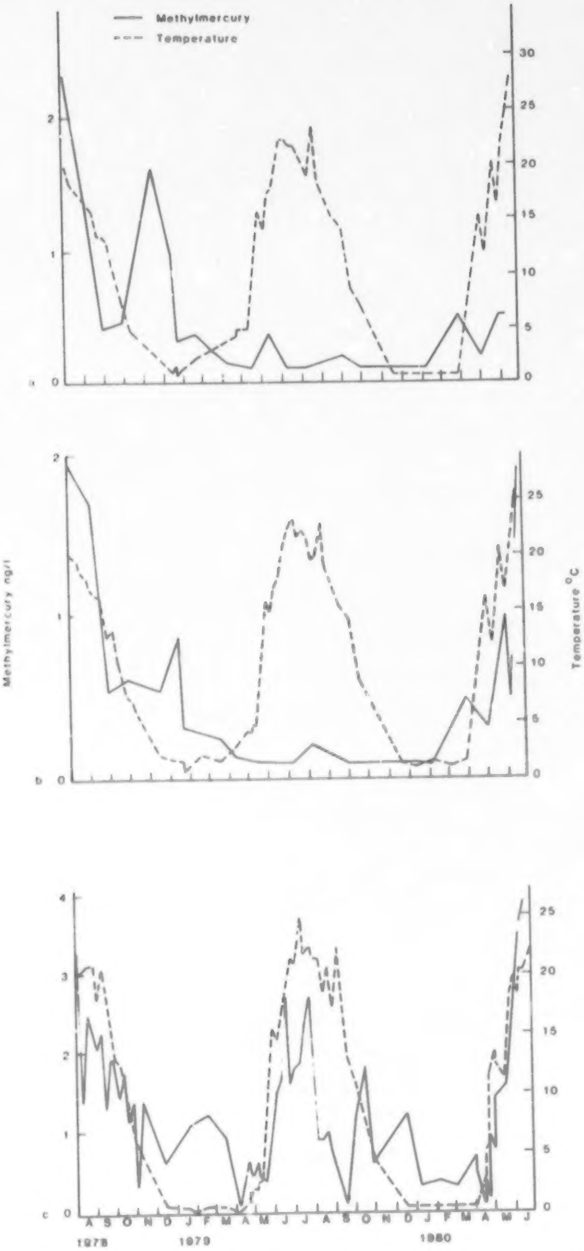


Figure 4.48 Methylmercury and temperature at selected sites in the Wabigoon River, August, 1978–June, 1980.

(a) Wainwright Dam inflow (4)
(b) Wainwright Dam outflow (5)
(c) Clay Lake (7)

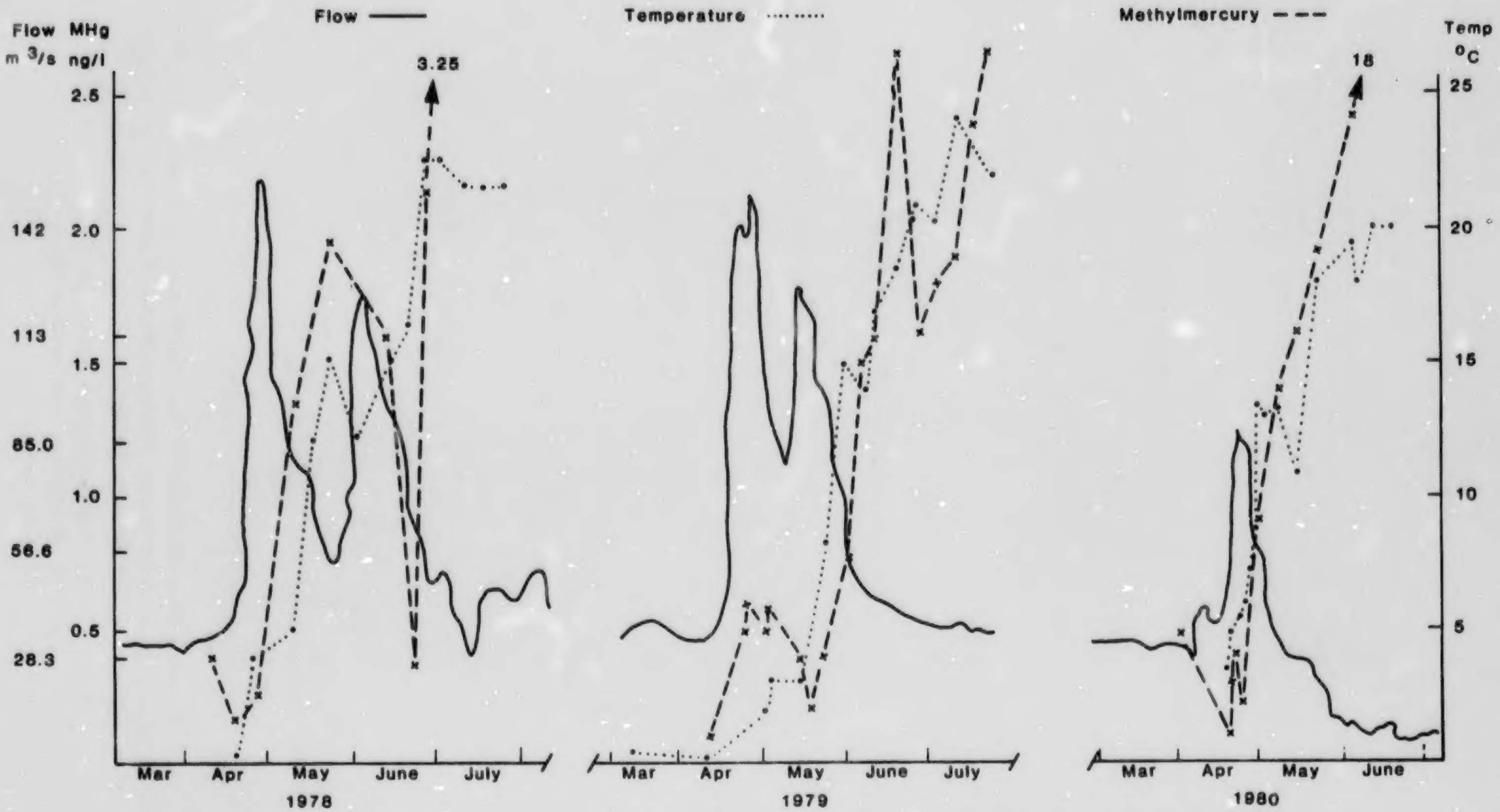


Figure 4.49 Methylmercury temperature and flow data, inflow to Clay Lake (site 7), during spring discharge in 1978, 1979 and 1980.

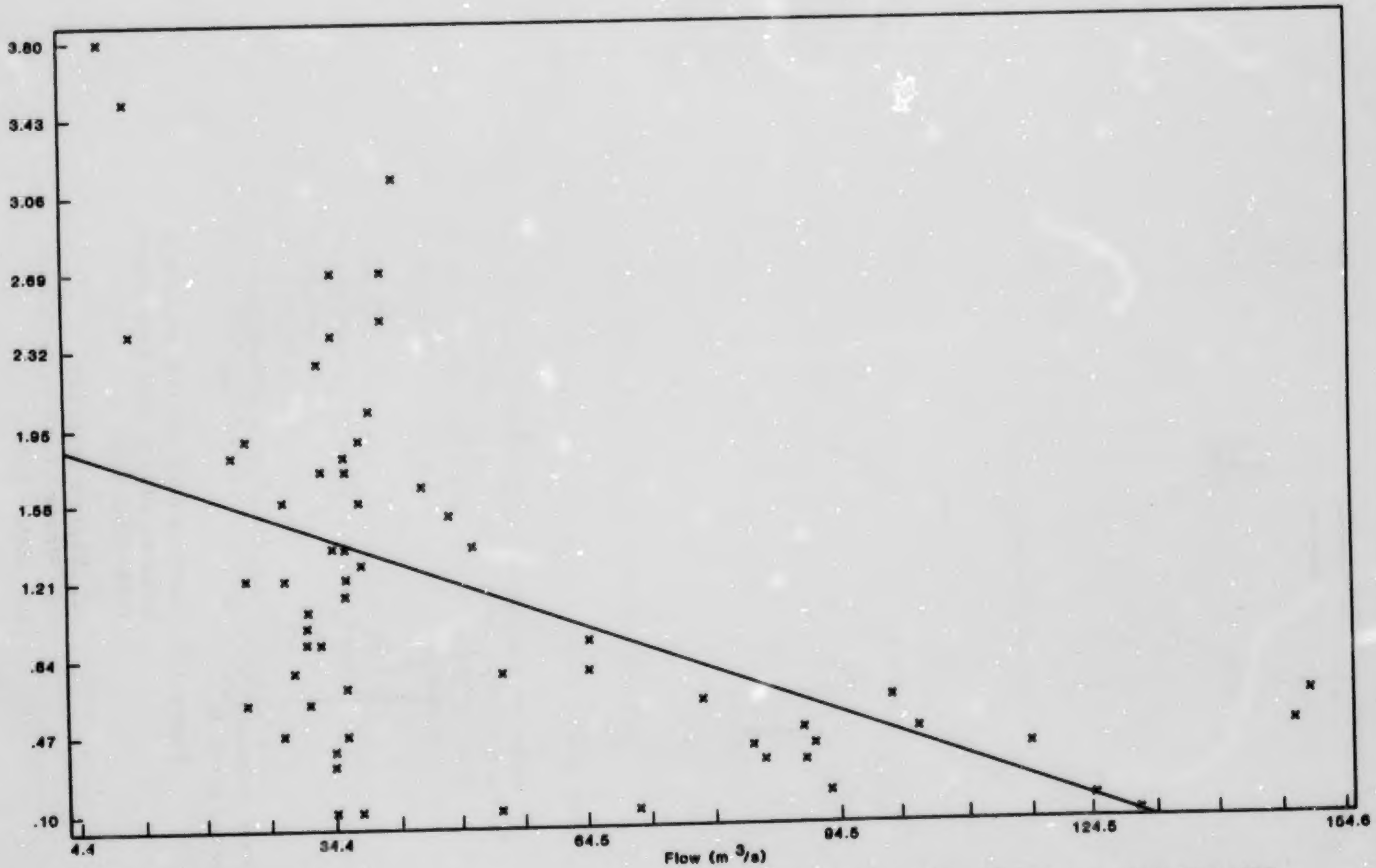


Figure 4.50 Relationship between Methylmercury concentrations and flow Clay Lake inflow (Site 7) Aug 1978-June 1980 ,r = -.48, p = .0001

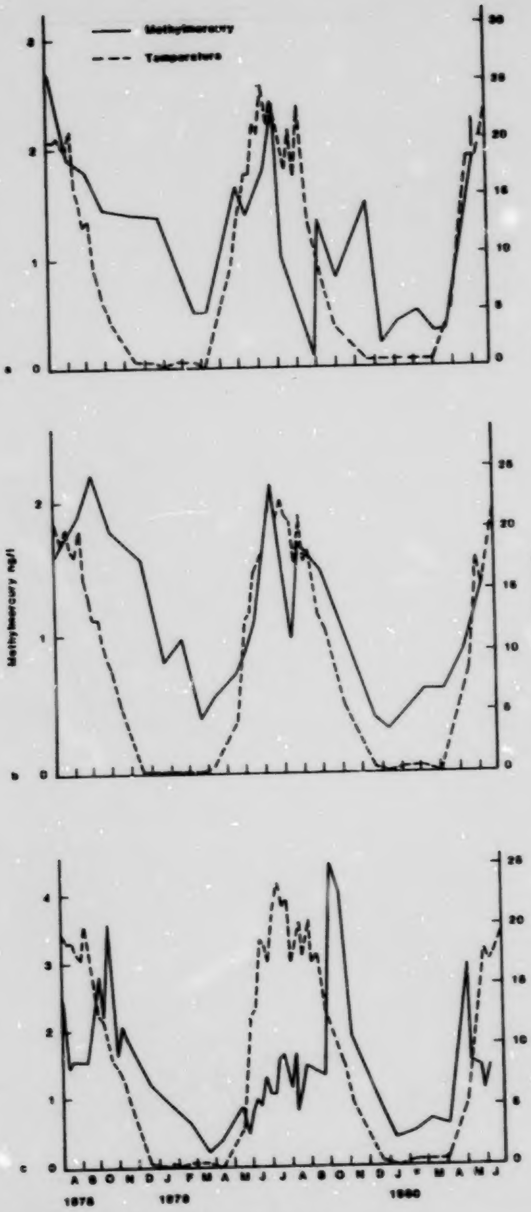


Figure 4.51 Methylmercury and temperature at selected sites in Clay Lake August, 1978-June, 1980.

(a) Eastern basin (8)
(b) Western basin epilimnion (9)
(c) outflow (10)

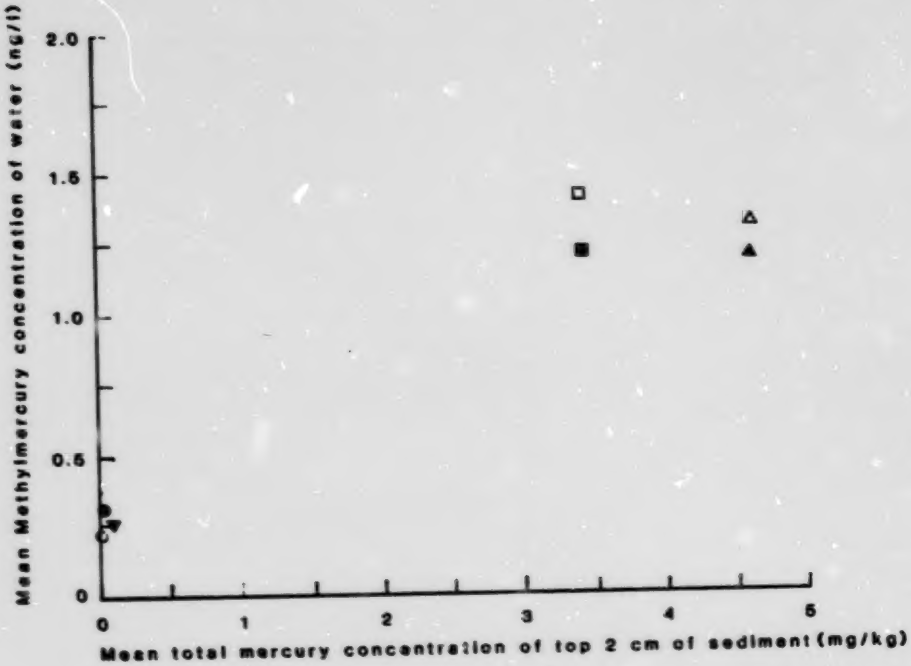


Figure 4.52 Relationship between methylmercury in water and total mercury in sediment at selected sites in the Wabigoon/English River system for 2 consecutive study periods of 12 months.

Open symbols: first study year
Closed symbols: second study year
○ ● Wabigoon Lake
□ ■ Clay Lake Eastern Basin
△ ▲ Clay Lake Western Basin
▼ English River upstream of Ball Lake (sediment from Maynard Lake)

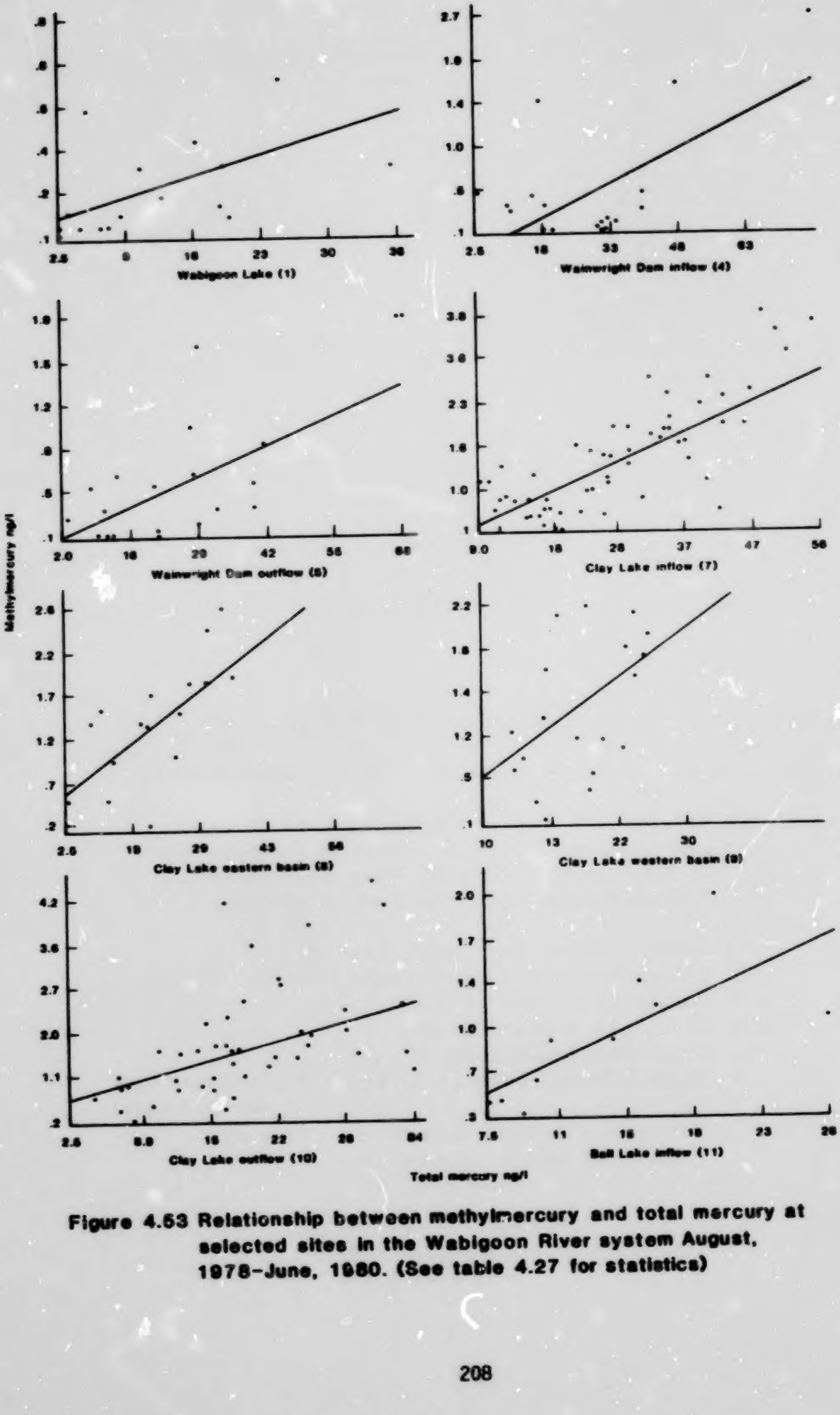


Figure 4.53 Relationship between methylmercury and total mercury at selected sites in the Wabigoon River system August, 1978–June, 1980. (See table 4.27 for statistics)

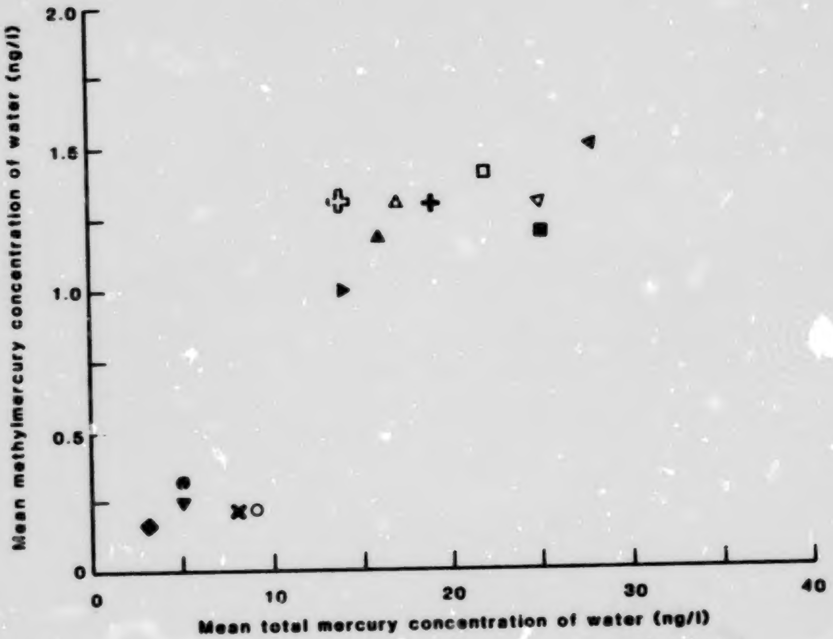


Figure 4.54 Relationship between methylmercury and total mercury in water at selected sites in the Wabigoon/English River system for 2 consecutive study periods of 12 months

Open symbols: first study year Aug 1978–July 1979
Closed symbols: second study year July 1979–June 1980

○ ● Wabigoon Lake
◆ Eagle River
□ ■ Clay Lake Eastern Basin
△ ▲ Clay Lake Western Basin
✙ ✚ Wabigoon River at Clay Lake outflow
◁ ◀ Wabigoon River at Clay Lake inflow
▶ Wabigoon River at Ball Lake inflow
▼ English River upstream of Ball Lake
✖ English River at Ball Lake outflow

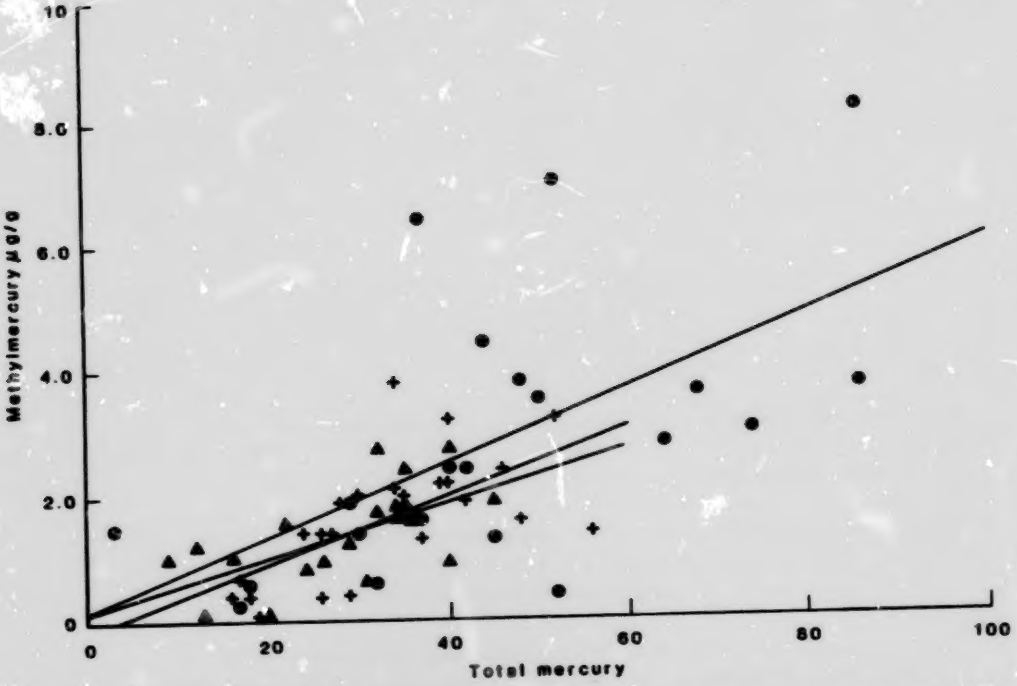


Figure 4.55 Relationship between methyl and total mercury at the inflow to Clay Lake under non-high flow conditions.

1978 +–+ r=.62 p<.01
1979 ▲–▲ r=.60 p<.01
1980 ●–● r=.59 p<.01

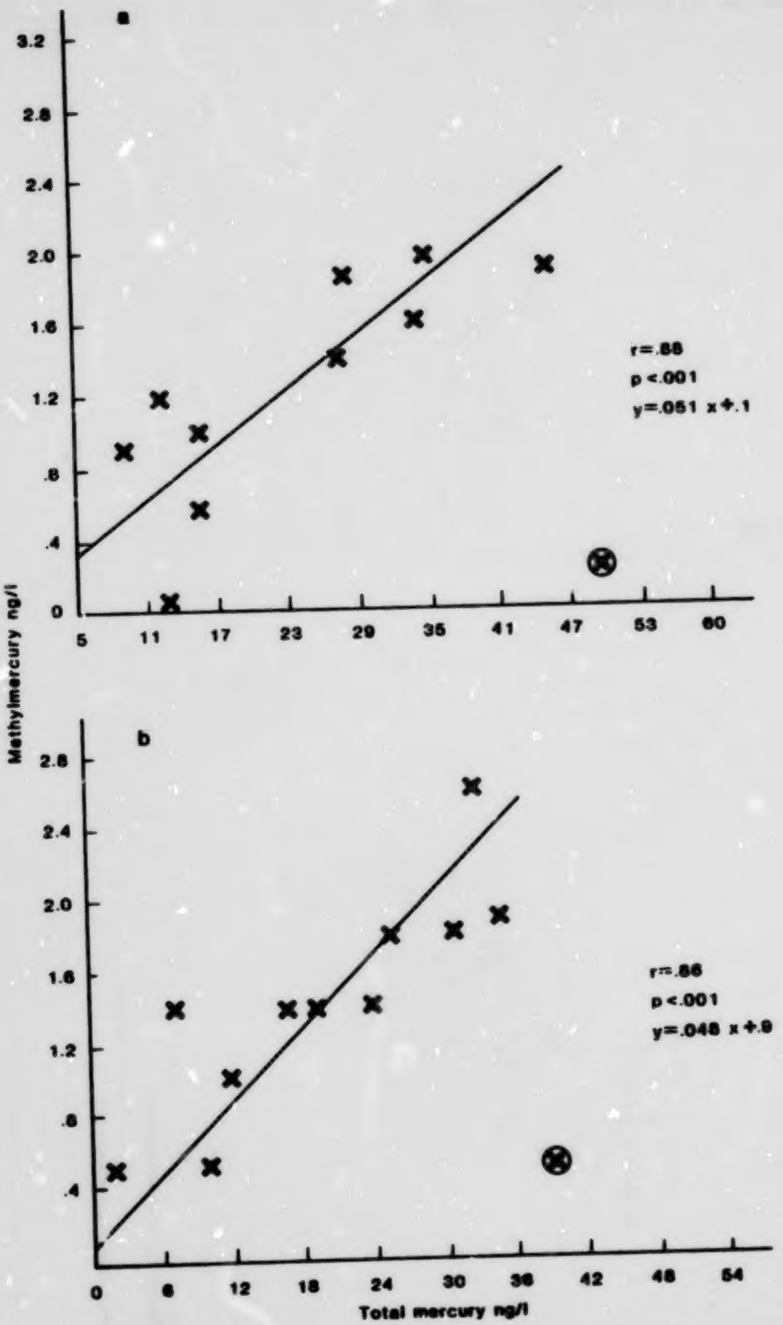


Figure 4.56 Relationship between Methylmercury and Total mercury from data collected monthly during the first study year. (a) Clay Lake inflow (b) Clay Lake eastern basin. Note-regression lines drawn omitting circled data pts. see text for explanation

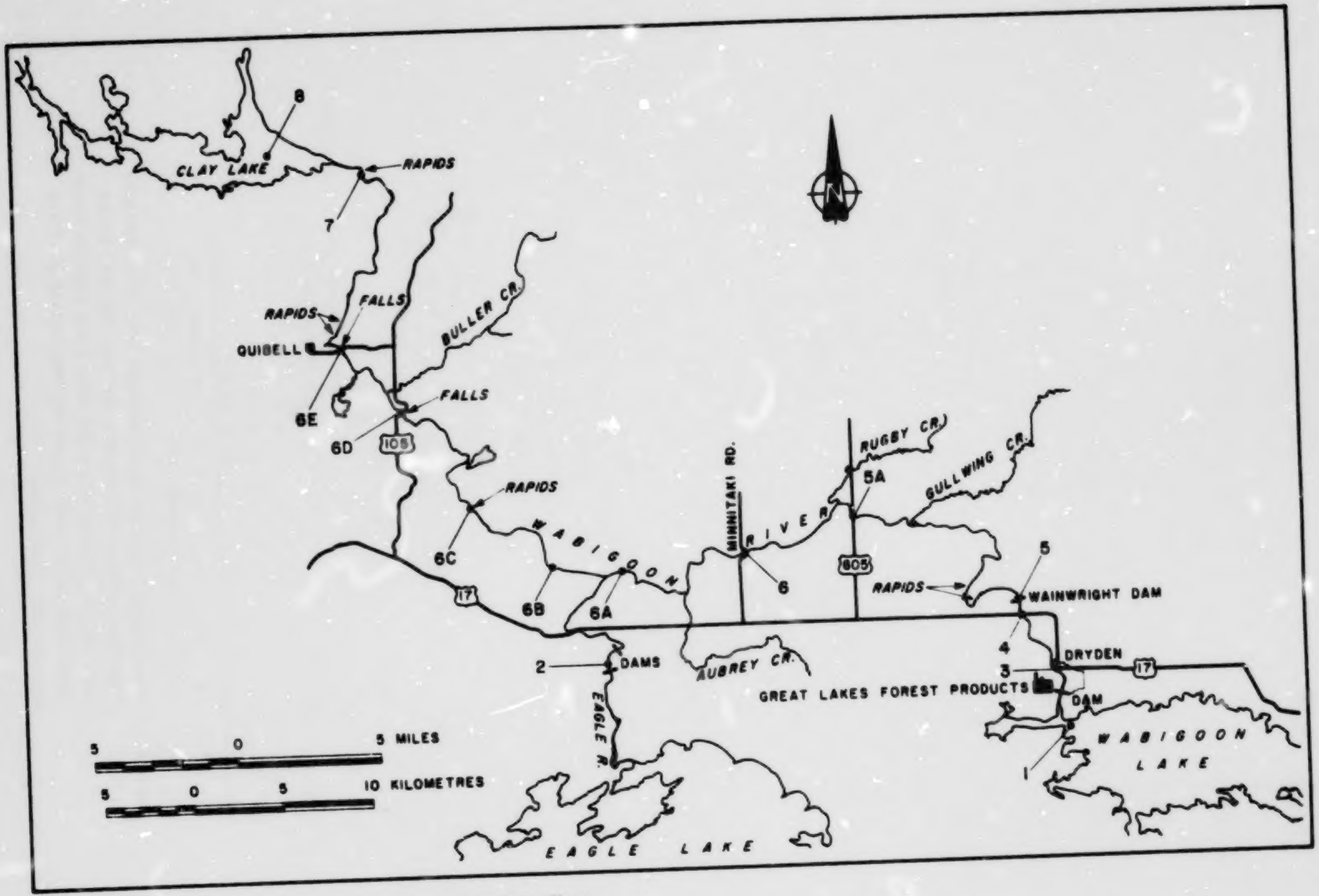

CLAY LAKE
8
RAPIDS
7
RAPIDS
FALLS
QUIBELL
BULLER CR.
FALLS
6E
6D
105
RAPIDS
WABIGOON RIVER
6C
6B
6A
17
MINNITAKI RD.
6
RUGBY CR.
5A
605
GULLWING CR.
5
RAPIDS
WAINWRIGHT DAM
4
DRYDEN
17
3
GREAT LAKES FOREST PRODUCTS
DAM
1
WABIGOON LAKE
AUBREY CR.
2
DAMS
EAGLE R.
EAGLE LAKE
5 0 5 MILES
5 0 5 10 KILOMETRES

Figure 4.57 Wabigoon River, intensive sampling sites.

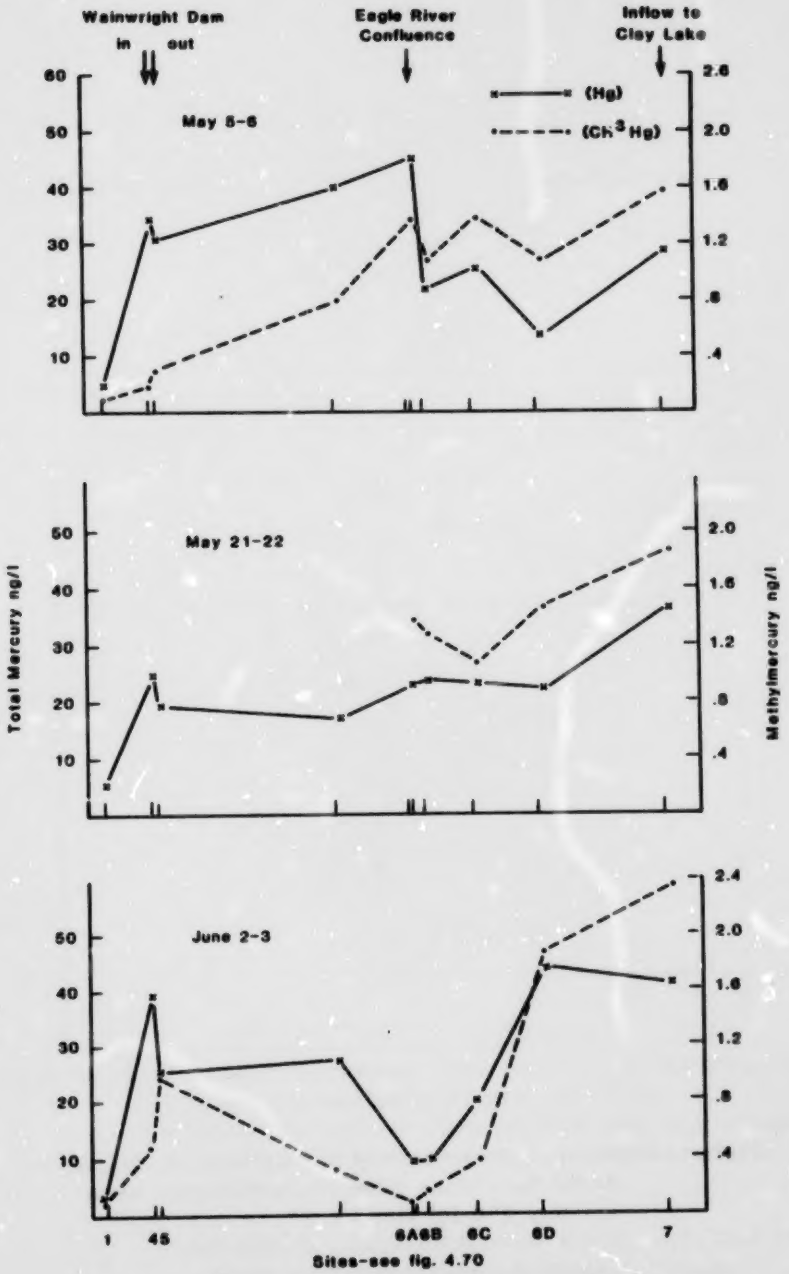


Figure 4.58 Total and Methylmercury concentrations Wabigoon River, Dryden to Clay Lake, 1980 (a) May 5-6 (b) May 21-22 (c) June 2-3

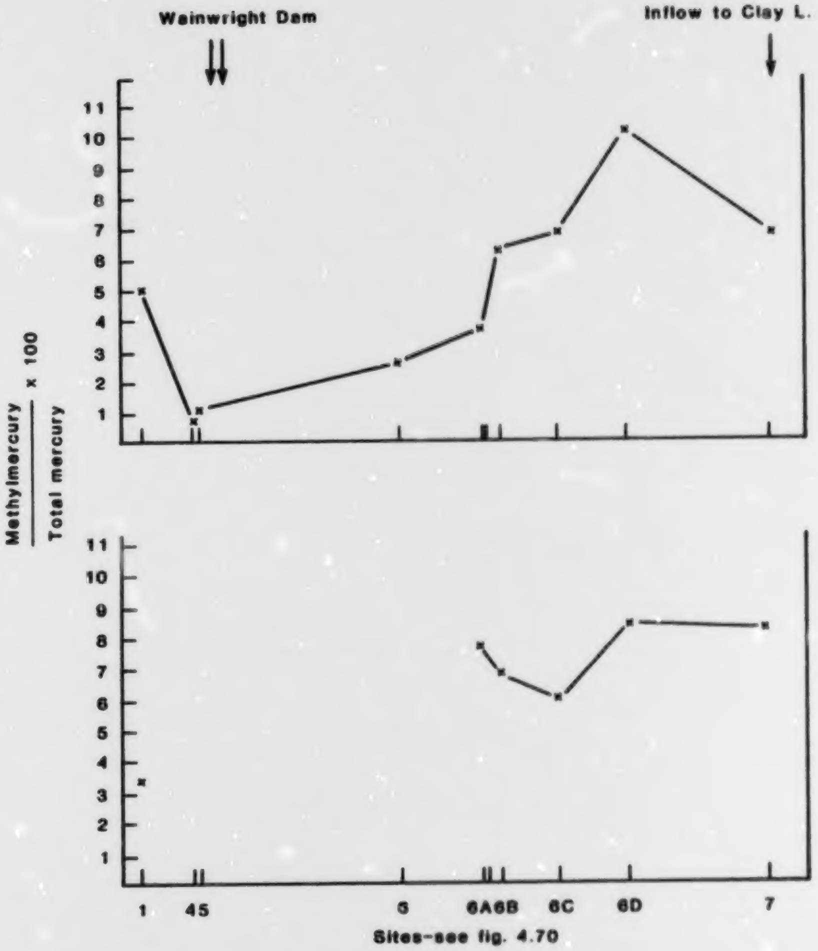


Figure 4.59 Ratio of Methylmercury to Total mercury (expressed as %) for various Sites in the Wabigoon River, 1980 (a) May 5-6 (b) May 21-22.

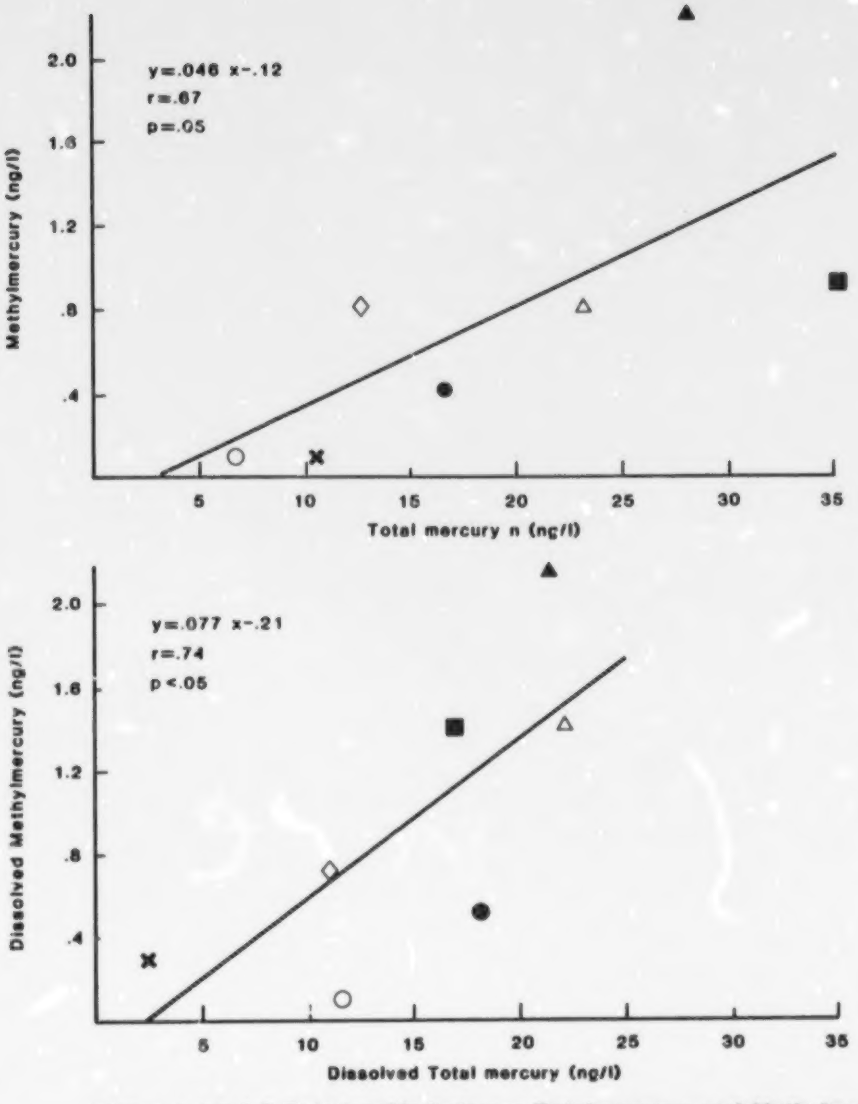


Figure 4.60 (a) Relationship between Total mercury and Methylmercury in the Wabigoon River System, July, 1979.
(b) Relationship between Total mercury dissolved mercury and dissolved Methylmercury in the Wabigoon River system, July 1979.

✖Wabigoon Lake, ○Eagle River, ●Wainwright Dam inflow,
■ Wainwright Dam outflow △Minnitaki, ▲Quibell,
◇ Clay Lake outflow

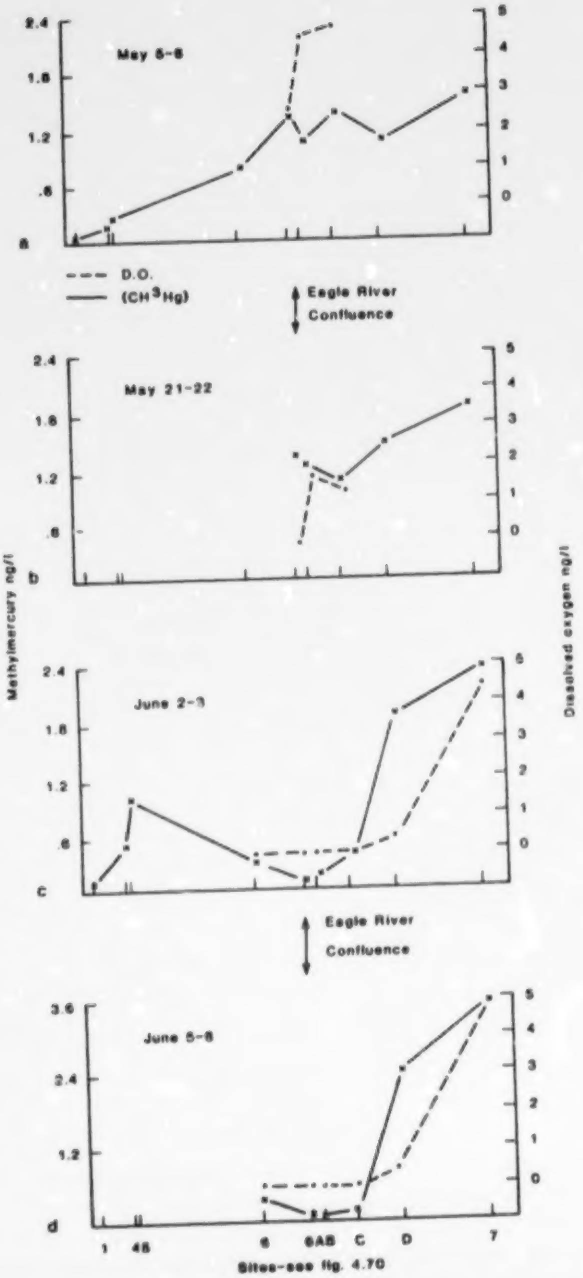


Figure 4.61 Methylmercury and dissolved oxygen concentrations, Wabigoon River, Dryden to Clay Lake, 1980.

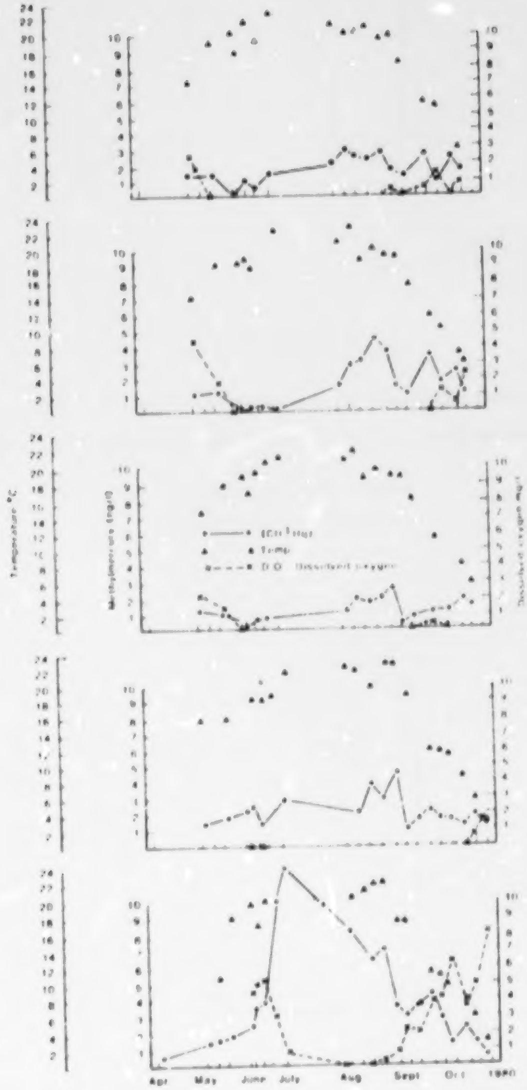


Figure 4.62 Methylmercury temperature and dissolved oxygen values for selected sites on the Wabigoon River, May–October, 1980.

(a) .5 km upstream o' Eagle River confluence, 6A
(b) 31 km downstream of Eagle River confluence, 6B
(c) 9.8 km downstream of Eagle River confluence, 6C
(d) Red Lake Hwy., 6D
(e) Clay Lake inflow
See Figure

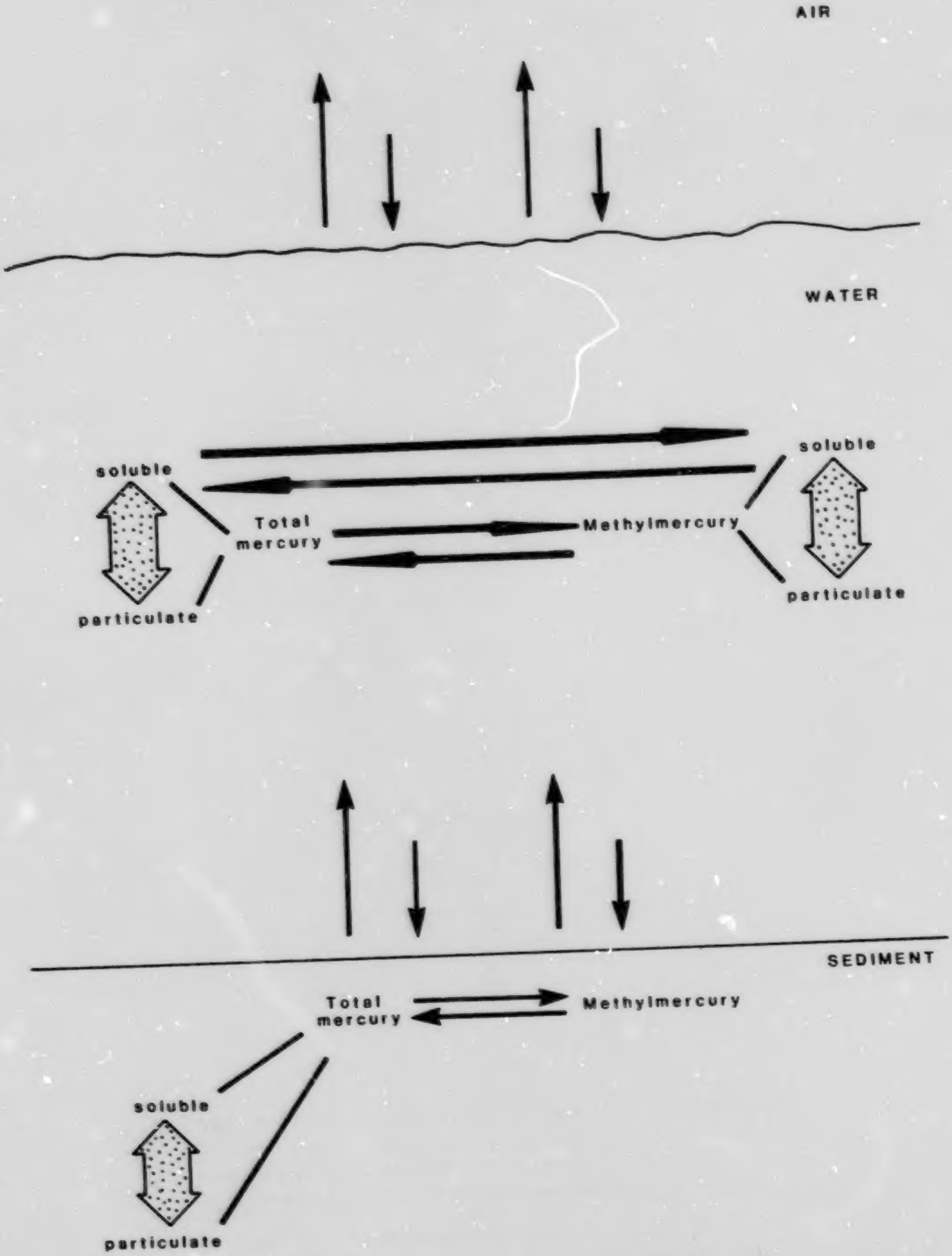

AIR
WATER
soluble
Total mercury
particulate
Methylmercury
soluble
particulate
SEDIMENT
Total mercury
Methylmercury
soluble
particulate

Figure 4.63 Selected components of the mercury cycle in a contaminate ecosystem, as inferred from studies on the Wabigoon River system.

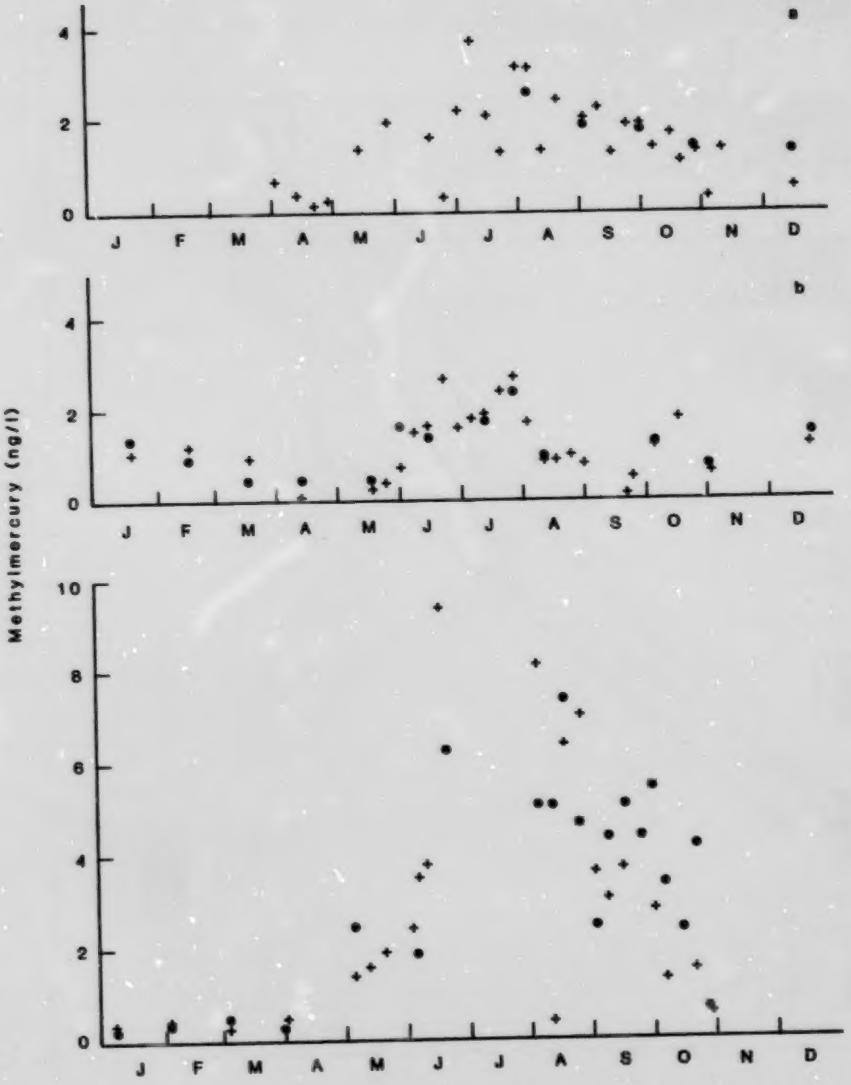


Figure 4.64 Methylmercury concentrations for the inflow to Clay Lake (+) and the eastern basin of Clay Lake (•) for (a) 1978 (b) 1979 (c) 1980.

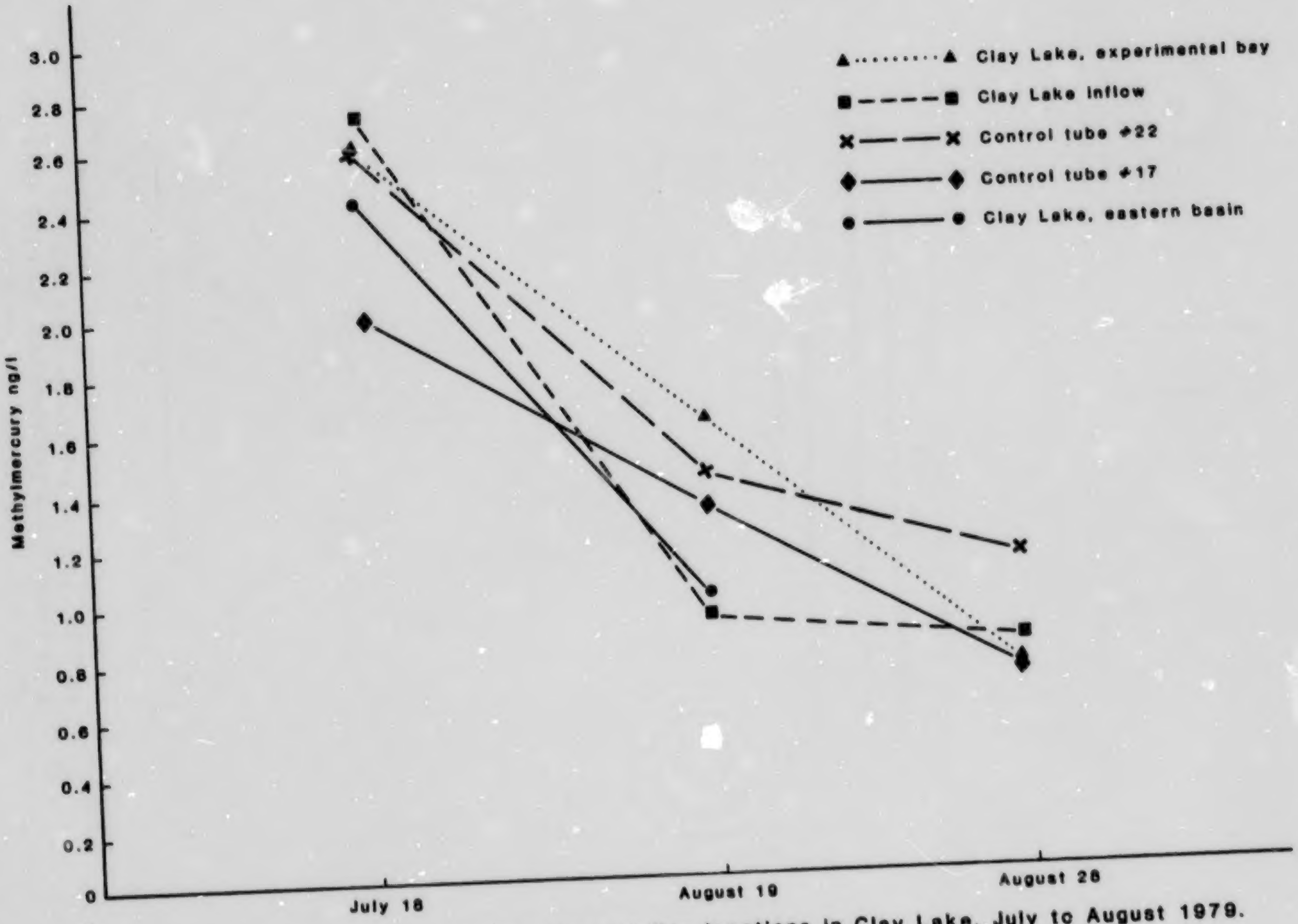


Figure 4.65 Methylmercury concentrations at five locations in Clay Lake, July to August 1979. Data from M. Turner (personal communication)

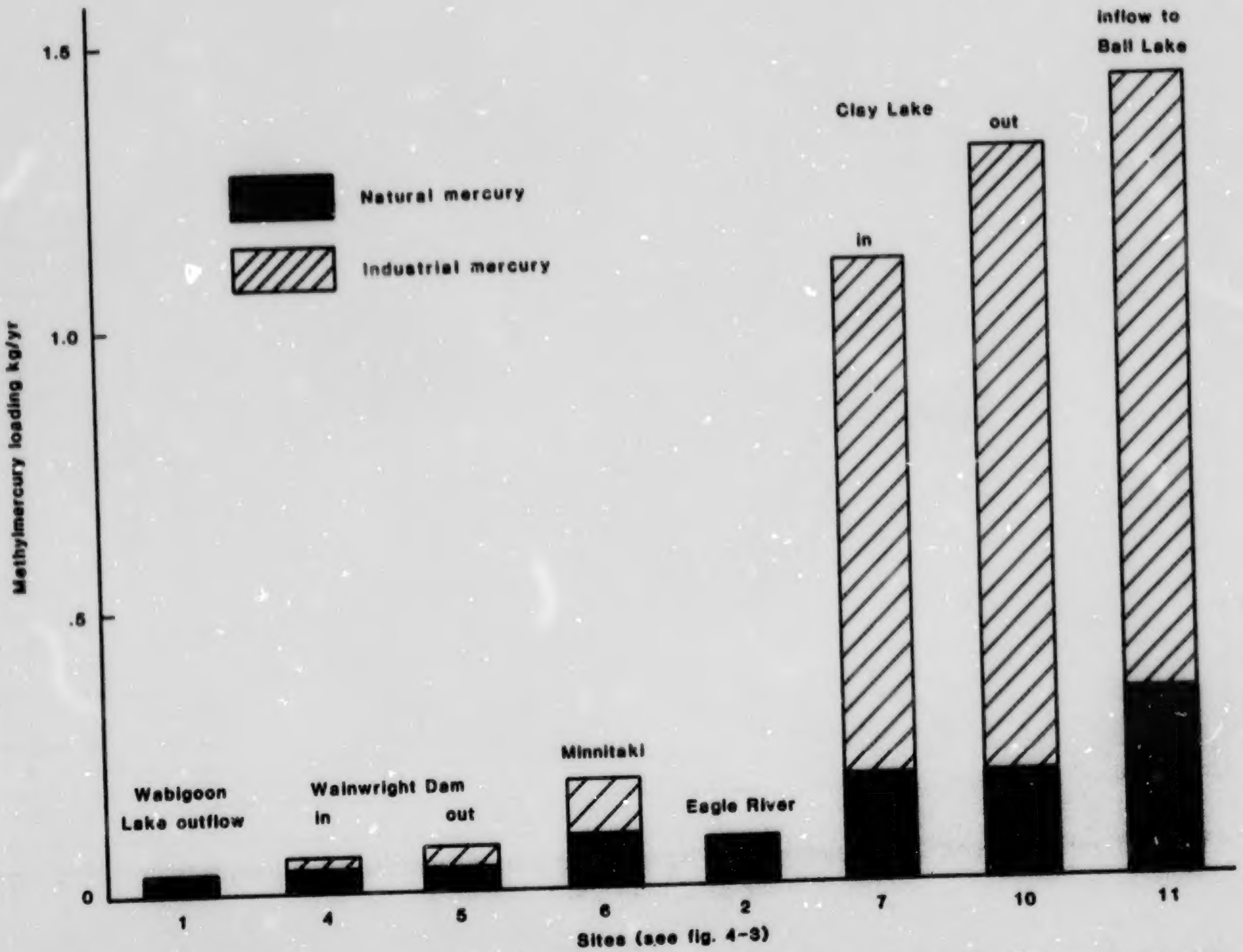


Figure 4.66 Natural and anthropogenically related Methylmercury loadings for various sites in the Wabigoon R. system Dryden to Ball Lake June 1979–June 1980.

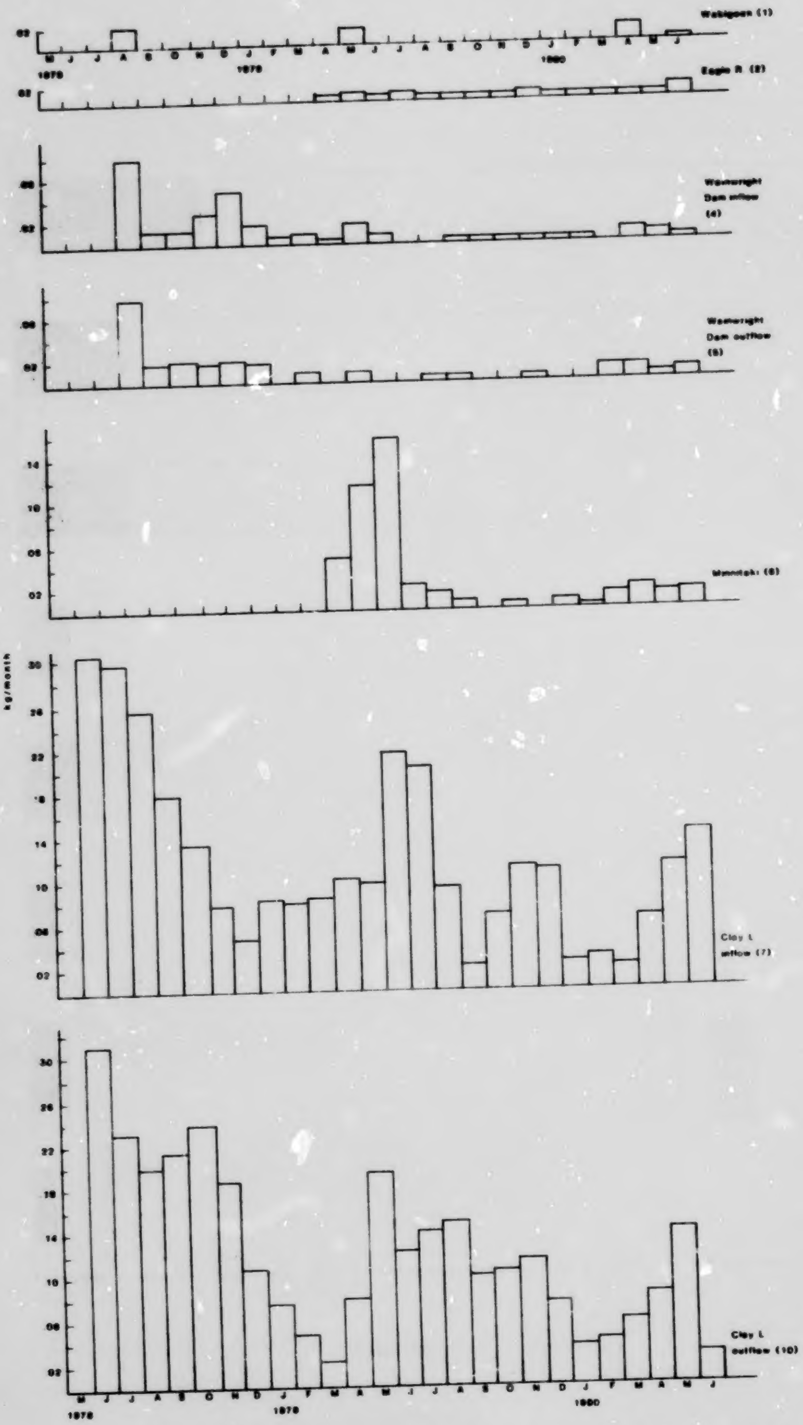


Figure 4.67 Monthly methylmercury loadings for selected sites in the Wabigoon River system, June, 1978-June, 1979.

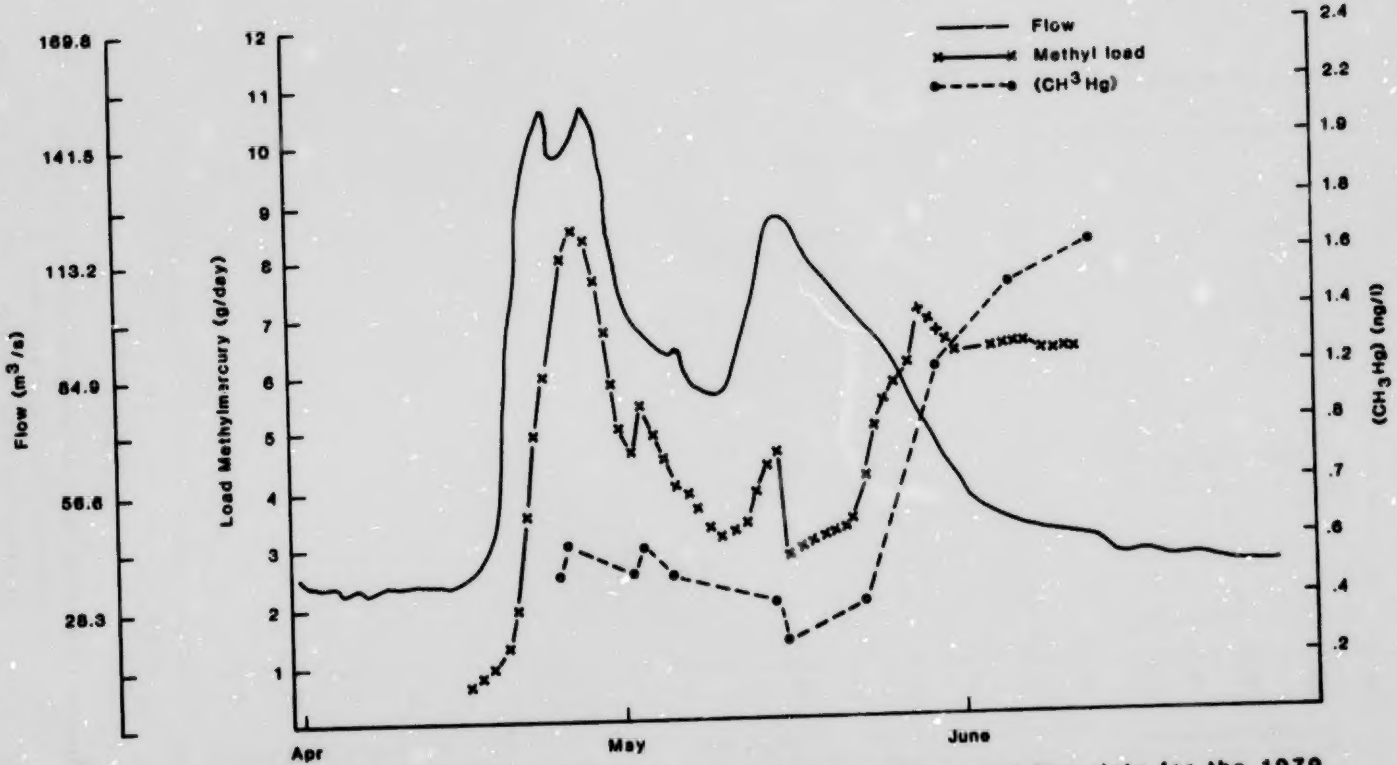


Figure 4.68 Methylmercury concentrations, loadings, and flow data for the 1979 spring runoff, Clay Lake inflow (site 7).

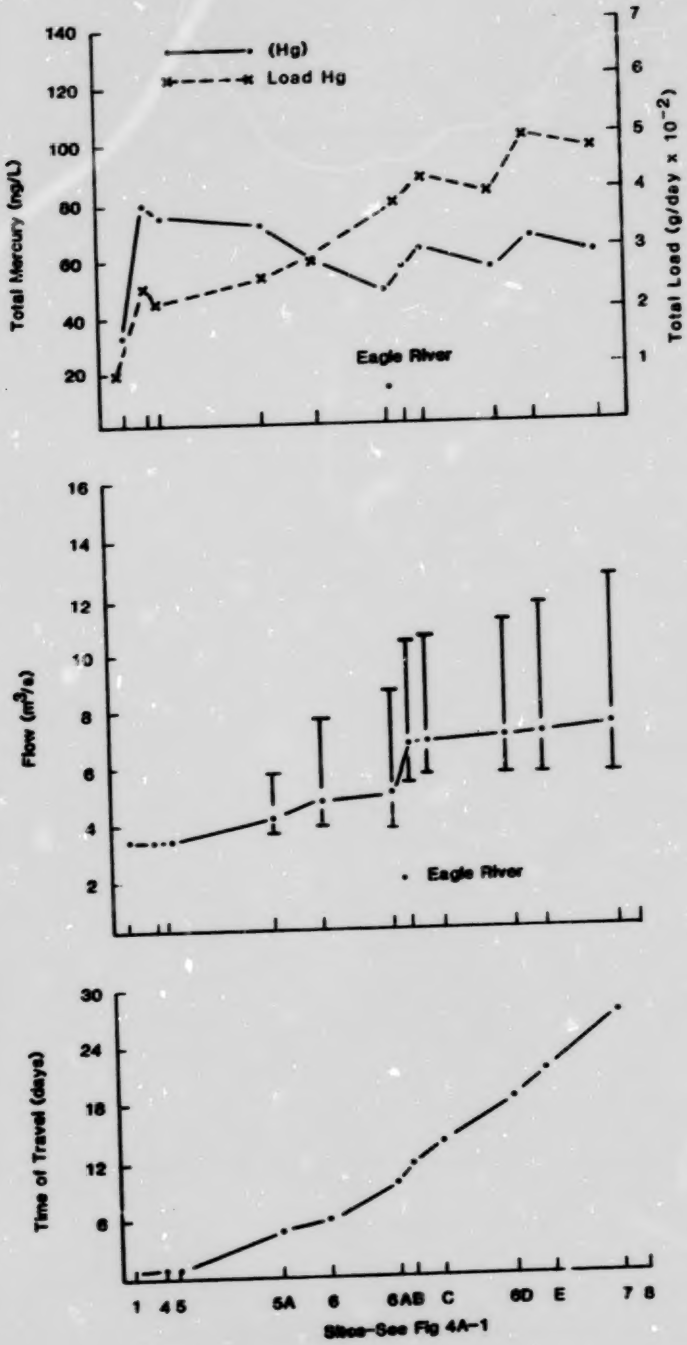


Figure 4.69 Mean total mercury concentrations and loadings, plus flow and time of travel for 10 sampling runs, August 4-October 20, 1980.

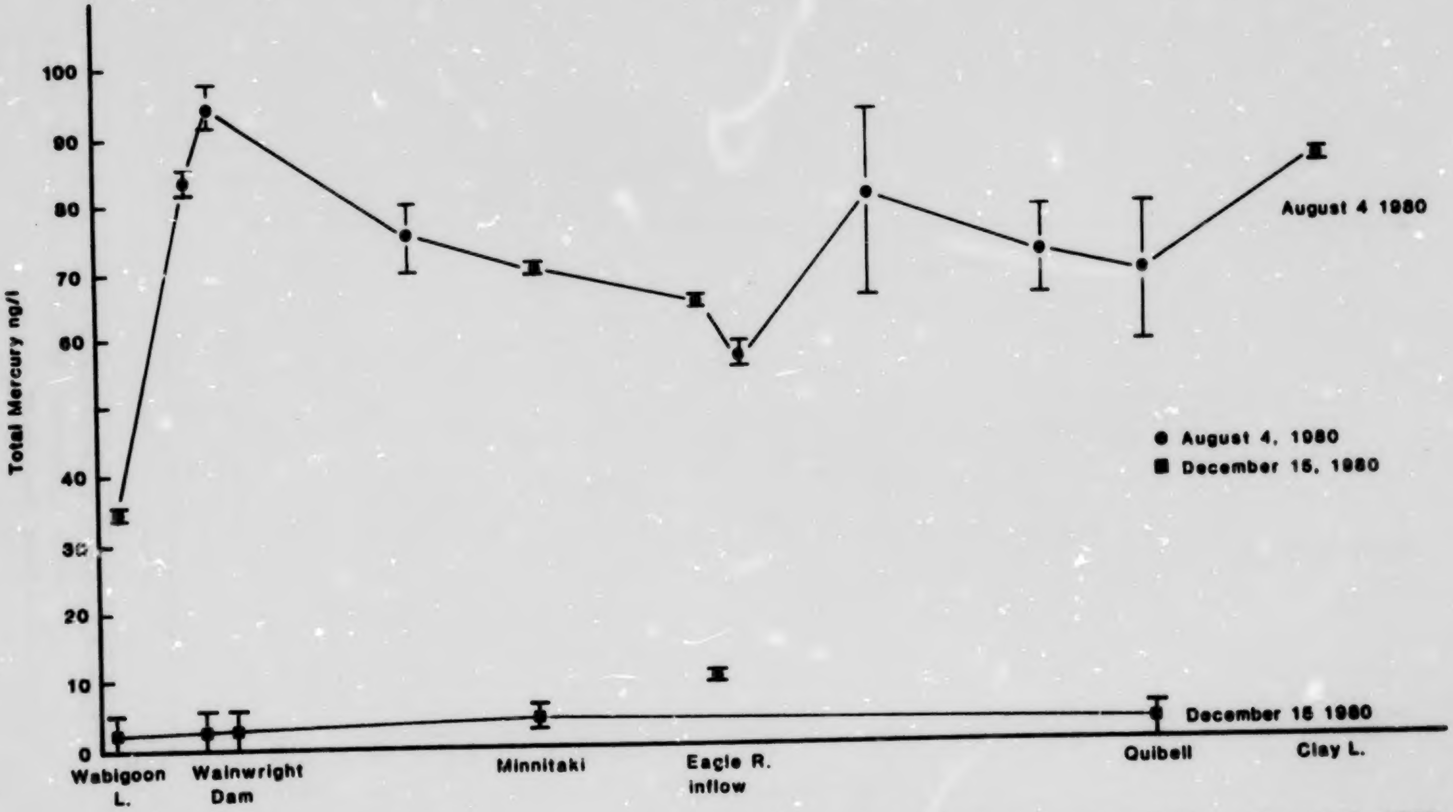


Figure 4.70 Mean and range of total mercury in duplicate samples from the Wabigoon River, August 4, 1980 and December 15, 1980.

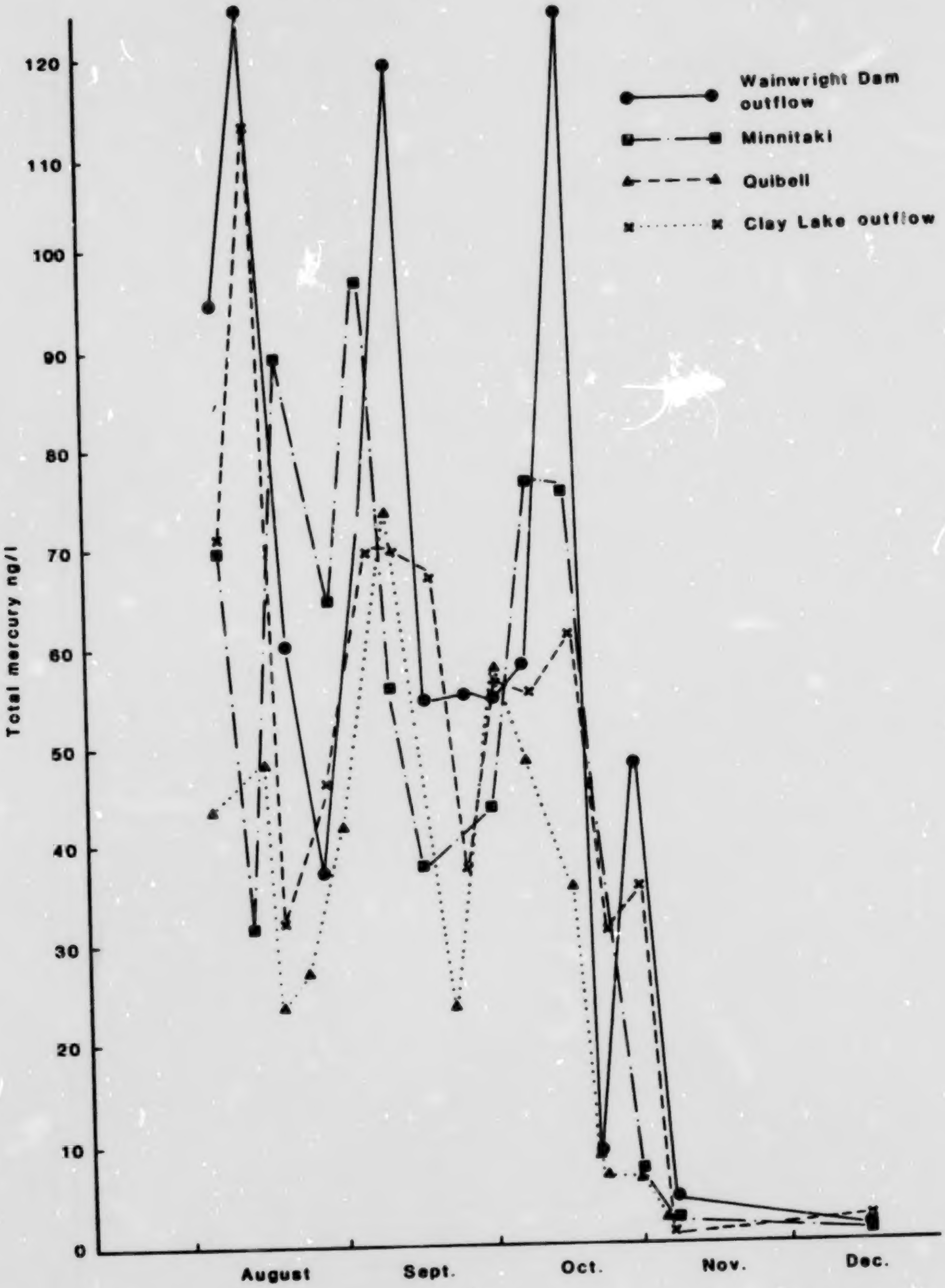


Figure 4.71 Mercury concentrations for four sites in the Wabigoon River system Dryden to Clay Lake outflow, August to December, 1980.

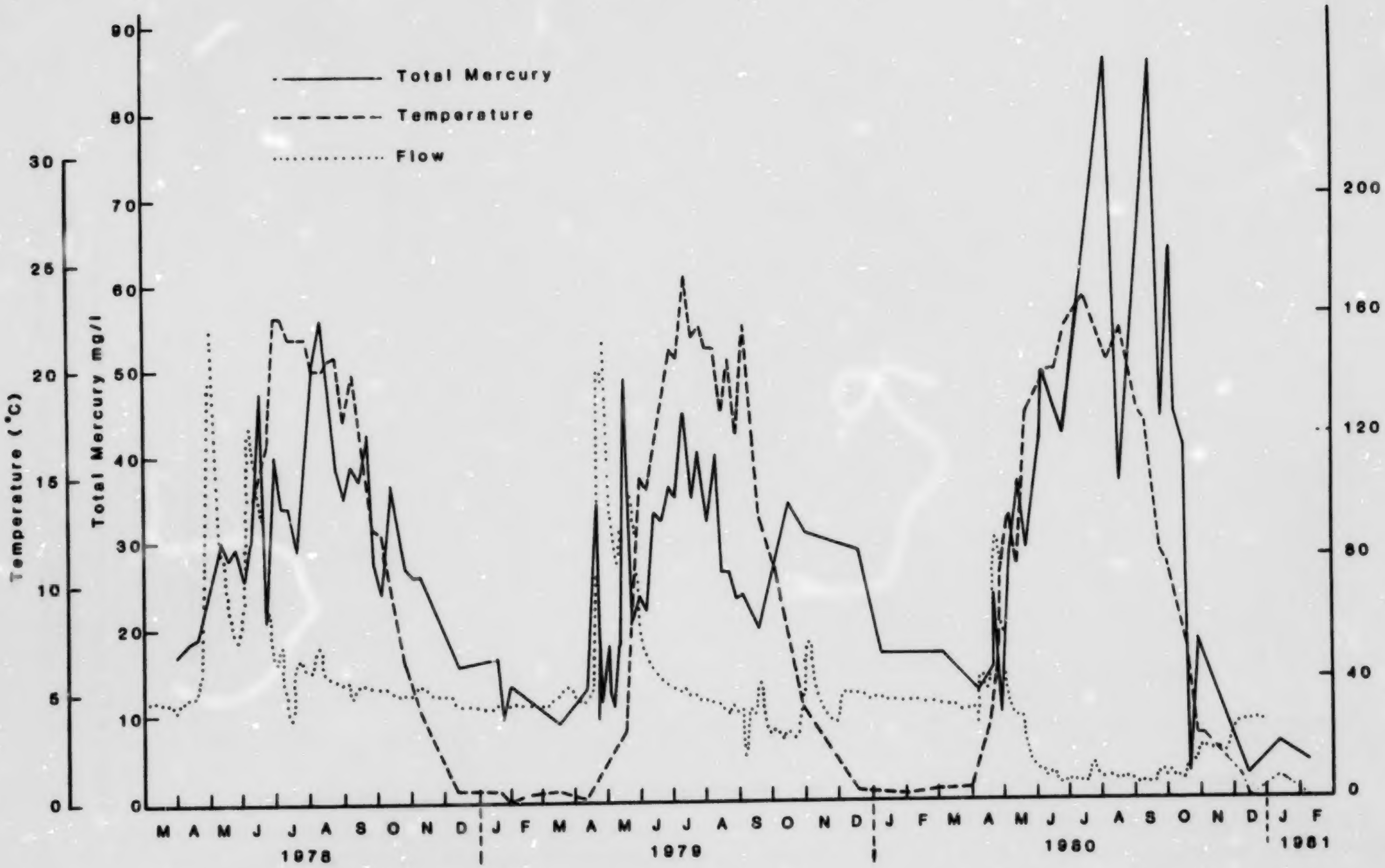


Figure 4.72 Total mercury and Temperature data, inflow to Clay Lake, Flow at Quibell March 1978–February 1981.

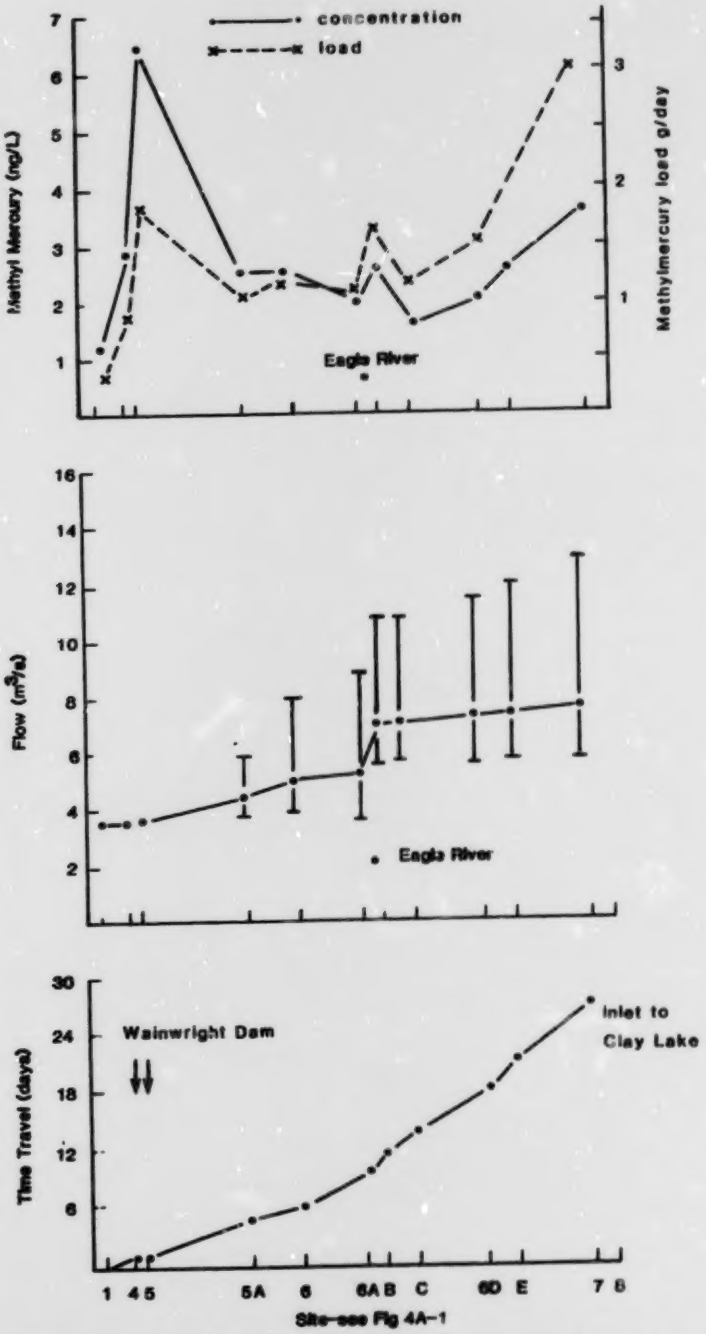


Figure 4.73 Mean methylmercury concentrations and loadings, plus flow and time of travel for 10 sampling runs, August 4-October 20, 1980.

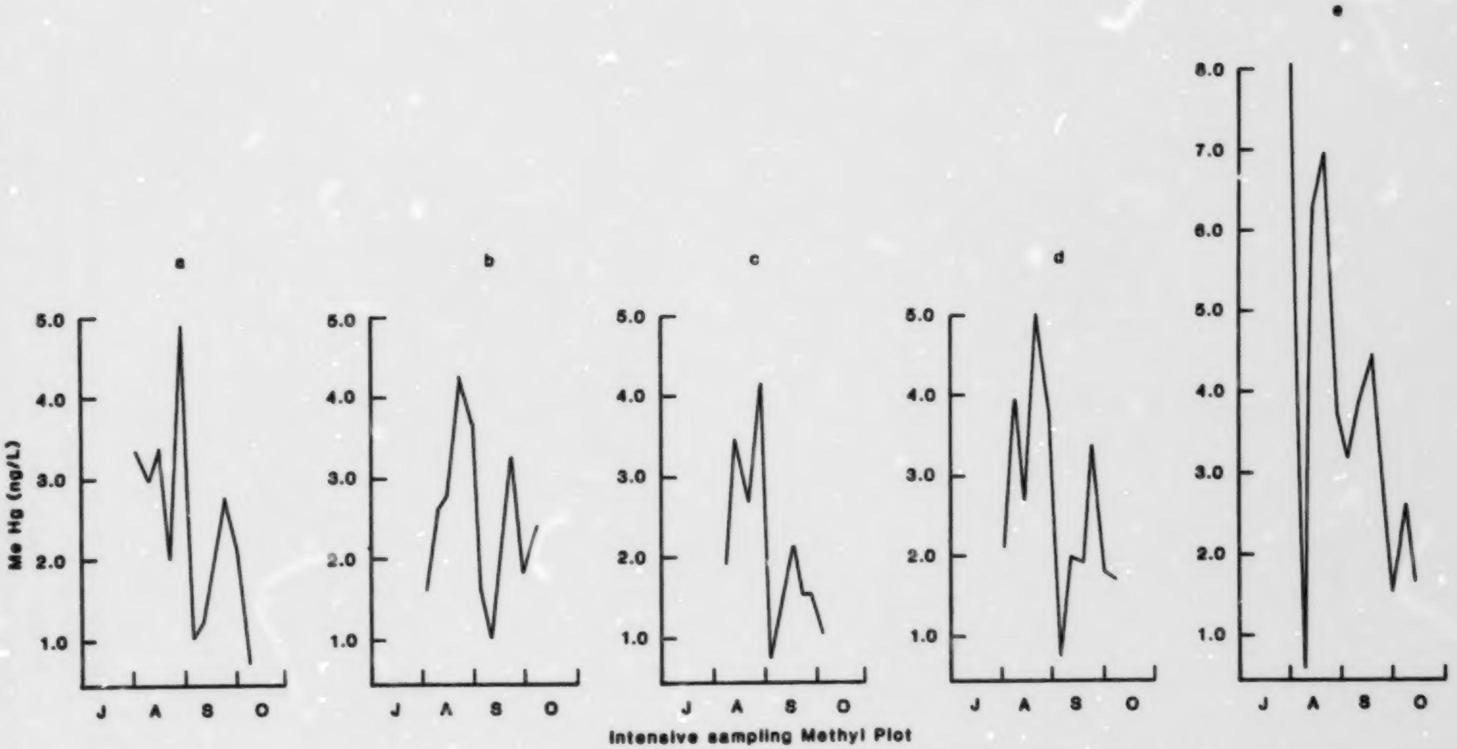
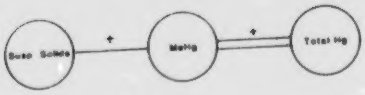
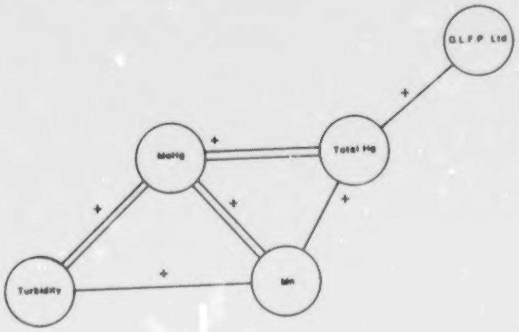


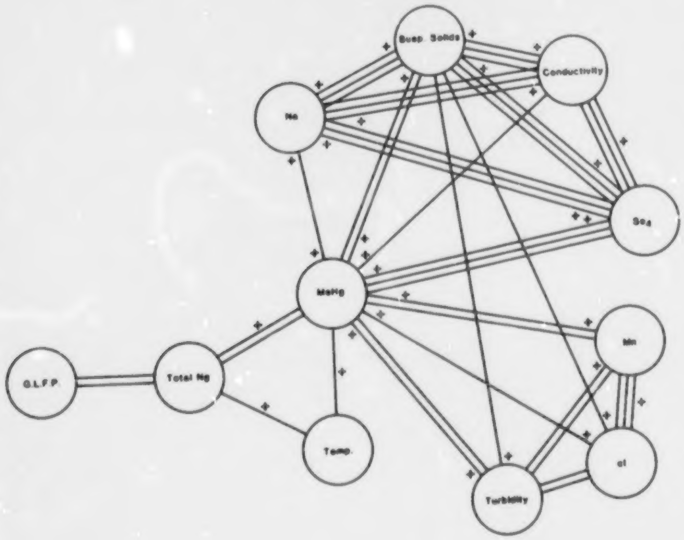
Figure 4.74 Methylmercury concentrations for selected sites in the Wabigoon River (a) at Eaton-Rugby Rd.-Site 5A (b) downstream of Eagle River-Site 6B (c) at Hwy No. 105-Site 6D (d) at Quibell-Site 6E and (e) at inflow to Clay Lake -Site 7, Aug 4-Oct 20 1980. Note Sites a and e are 20 travel days apart.


Susp. Solids
MeHg
Total Hg

Wabigoon Lake

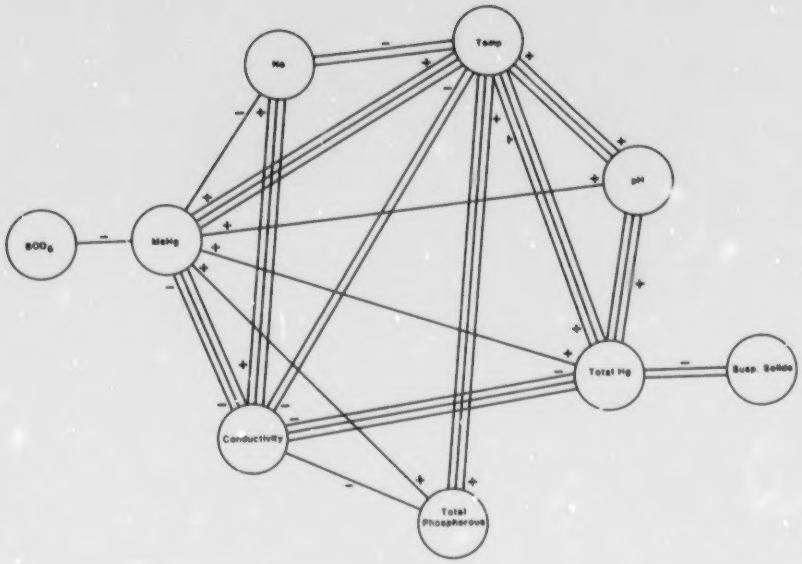

G.L.F.P. Ltd
MeHg
Total Hg
Turbidity
Mn

Wainwright Dam inflow

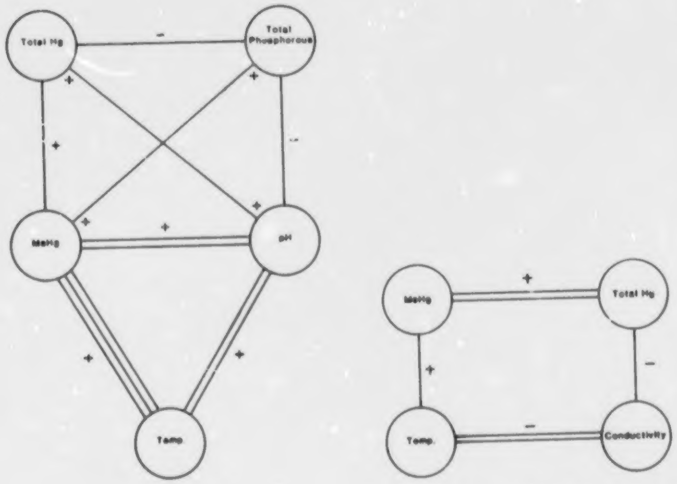

Susp. Solids
Conductivity
Na
So4
MeHg
Mn
G.L.F.P.
Total Hg
Temp.
Cl
Turbidity

Wainwright Dam outflow

Figure 4.75 Correlellograms between methylmercury, total mercury and other parameters. (Total Hg=total mercury, MeHg=methylmercury, Susp. Solids=suspended solids, Temp.=temperature, Mn=manganese, Fe=Iron, Cl=chloride, SO_4=sulphate, Na=sodium)

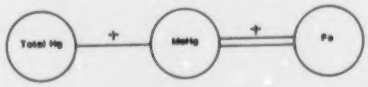

Na
Temp
pH
BOD5
MeHg
Total Hg
Susp. Solids
Conductivity
Total Phosphorous

Clay Lake-eastern basin


Total Hg
Total Phosphorous
MeHg
pH
Temp.
MeHg
Total Hg
Temp.
Conductivity

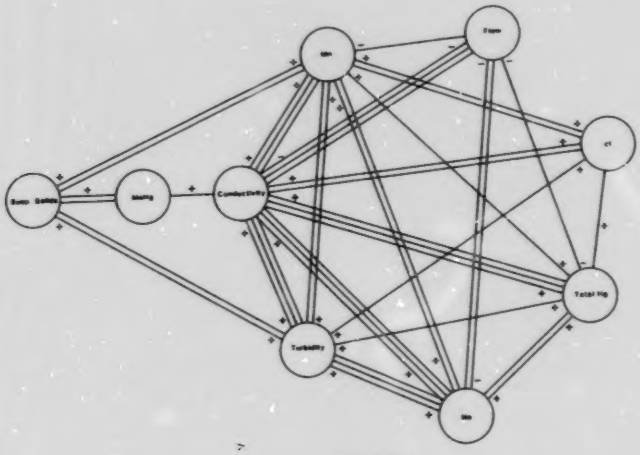
Clay Lake western basin

Clay Lake outflow

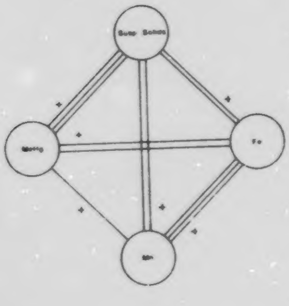

Total Hg
MeHg
Fe

Wabigoon River inflow to Ball Lake

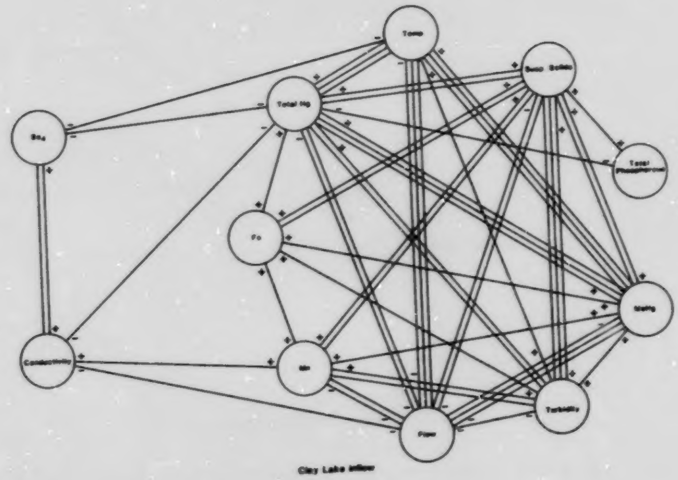
Figure 4.75 Correlellograms between methylmercury, total mercury and other parameters.


Susp. Solids
MeHg
Conductivity
Mn
Flow
Cl
Total Hg
Turbidity
+
-

Wabigoon River at Minnitaki


Susp. Solids
MeHg
Fe
Mn
+
-

Eagle River


Temp
Susp. Solids
Total Hg
SO4
Total Phosphorus
Fe
MeHg
Conductivity
Mn
Turbidity
Flow
+
-

Clay Lake inflow

Figure 4.75 Correlellograms between methylmercury total mercury and other parameters.

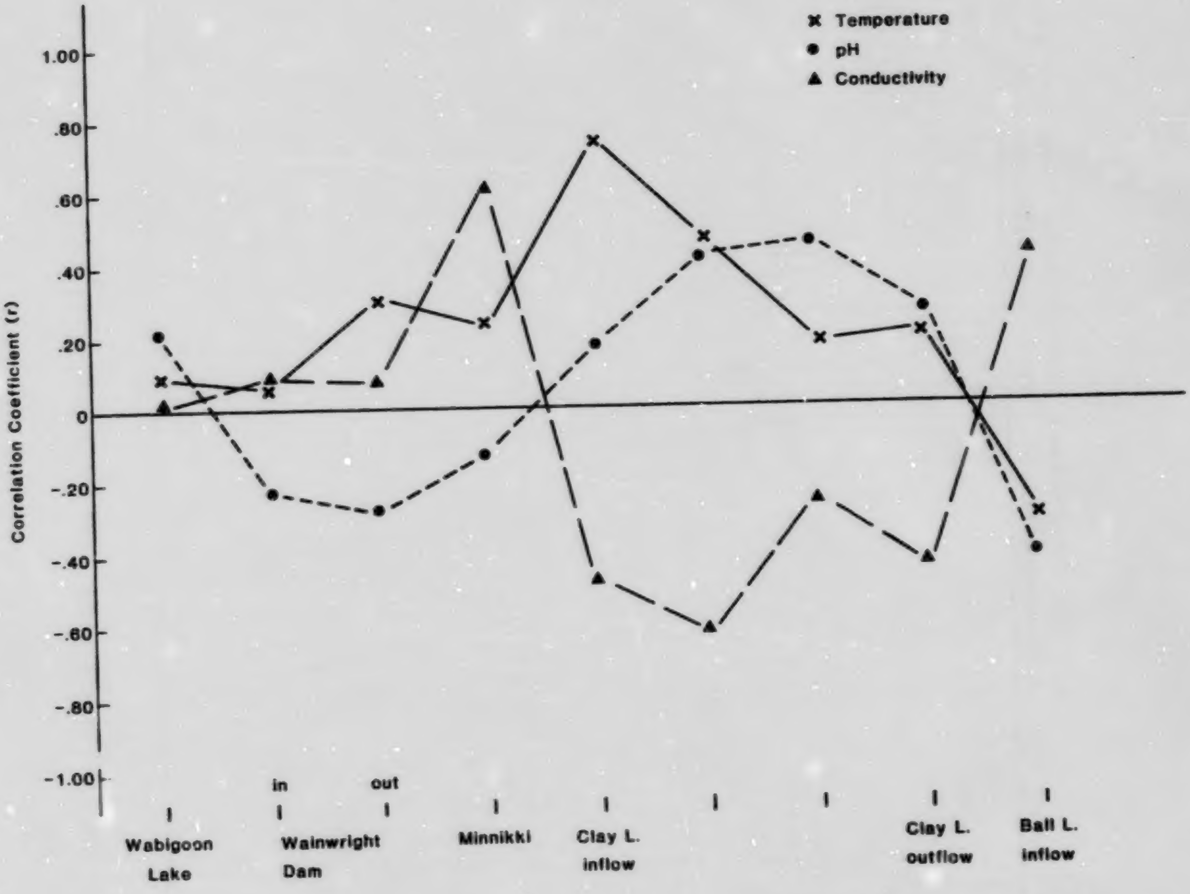


Figure 4.76 Correlation coefficients between total mercury and other parameters in the Wabigoon River system. (For statistical significance see Table 4.30)

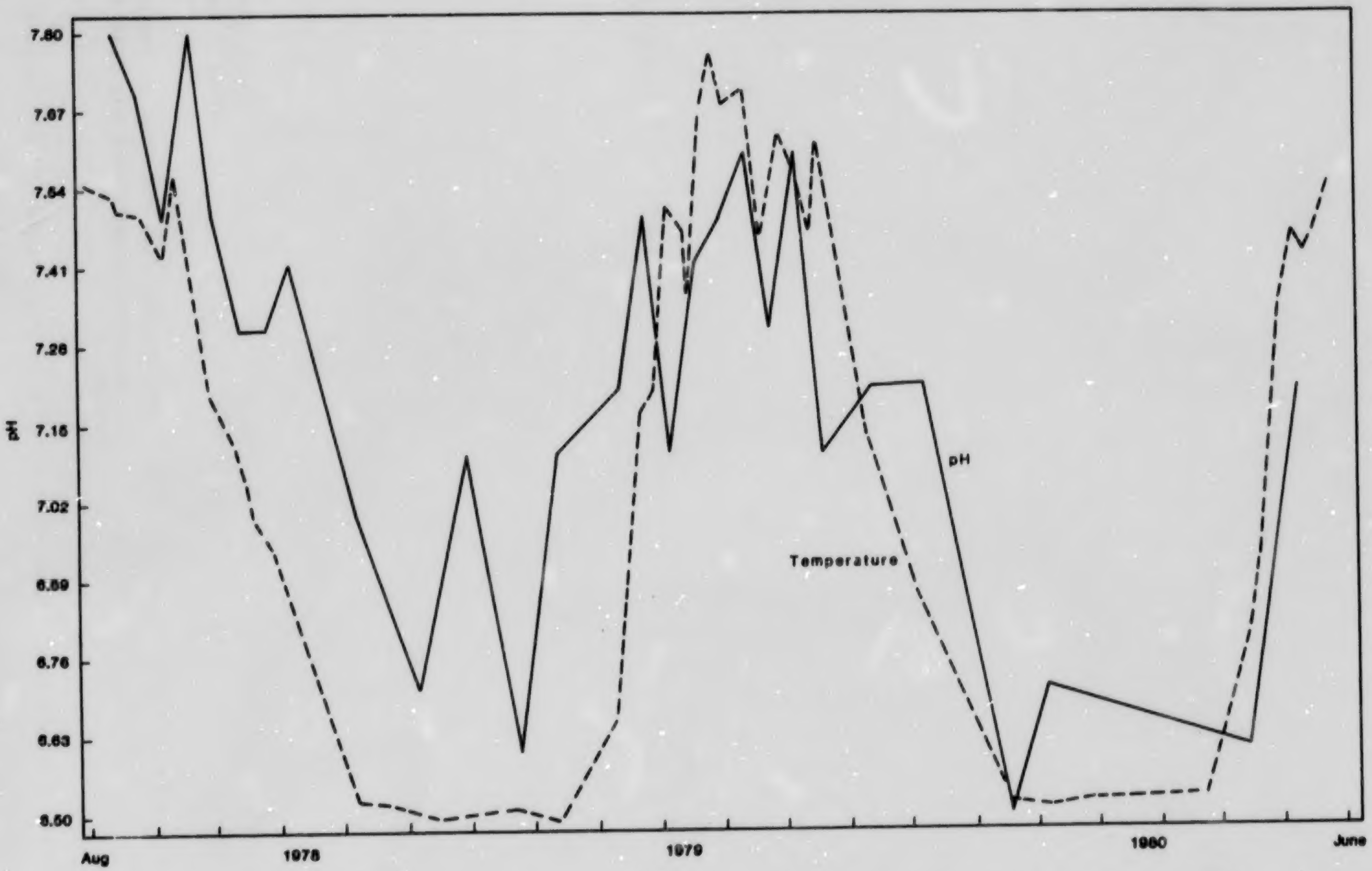


Figure 4.77 pH and temperature in water sampled at Clay Lake outflow (site 10), August 1978 to June 1980.

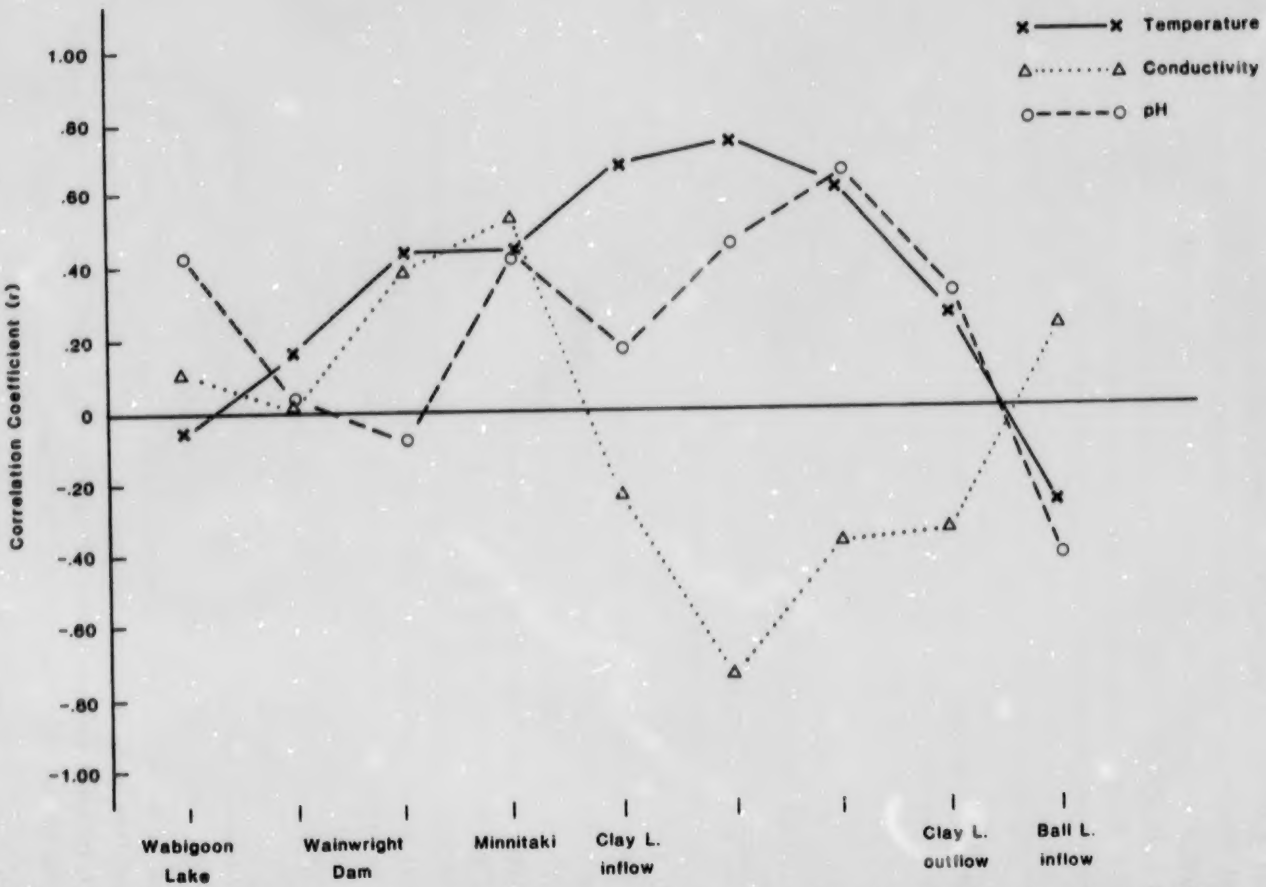


Figure 4.78 Correleation coefficients between methylmercury and other parameters in the Wabigoon River system. (For statistical significance, see Table 4.31)

5. MERCURY IN BIOTA

5.1 INTRODUCTION

Industrial losses of mercury to freshwater and marine environments in Japan, Sweden, Finland and Canada have resulted in the accumulation of high body burdens of mercury in aquatic organisms (Yoshida, et al., 1967; Johnels, 1967; Miettinen, 1969; Fimereite, et al., 1971). In Canada, Bligh (1970) reported excessively elevated mercury in fish from the Wabigoon River system, downstream from a mercury-cell chlor-alkali plant. Even several years after mercury discharges from this source declined substantially, mercury levels in biota from the system remained elevated (Armstrong and Hamilton, 1973; Bishop and Neary, 1974; Parks et al., 1980).

Of the total mercury in the edible portion of fish, 85 to 95 percent comprises methylmercury (Hannerz, 1968; Miettinen, 1969; Armstrong and Hamilton, 1973; Uthe, et al., 1972; D'Itri, 1973; Bishop and Neary, 1974; de Frietas, et al., 1977). Inorganic mercury is located in the viscera (de Freitas, et al., 1977). For fish to accumulate methylmercury, the industrially discharged inorganic mercury must be transformed to the organic or methyl form (methylation), and then be accumulated through the aquatic food web and/or absorbed directly from water.

There is conflicting evidence about the ability of fish to methylate inorganic mercury "in vivo" and the significance of this process to the total mercury body burden of fish. Several investigations indicate that this process is of little significance (Huckabee, et al., 1978; Pennachioni, et al., 1976). However, methylation in the surface slime of fish was reported by Jernelov (1972), and Rudd, et al. (1980) demonstrated that the intestines of six fresh water fish species could methylate pure inorganic mercury ($HgCl_2$). The importance of this process to the total mercury body burden was not assessed, however. We believe that "in vivo" methylation accounts for a relatively small proportion of the body burden (Section 6). Fish and other aquatic organisms accumulate methylmercury by direct absorption from water and consumption of mercury-containing food. Water-borne methylmercury may be absorbed through skin or gill membrances (Hannerz, 1968; Johnels, 1967; Wobeser, et al., 1970; D'Itri, 1973; Jernelov and Lan, 1971). Accumulation through the food chain occurs by ingestion and subsequent absorption (Jernelov and Lan, 1971; D'Itri, 1973; Armstrong and Hamilton, 1973; Huckabee, et al., 1975). Most of the methylmercury absorbed by fish from either pathway is retained and eliminated slowly (Hannerz, 1968; Miettinen, 1969; Uthe, et al., 1972; Armstrong and Hamilton, 1973; de Freitas, et al., 1977). Time of exposure and factors such as methylmercury concentrations in water, water temperature and food availability affect mercury uptake (Norstrom, et al., 1979; de Freitas, et al., 1977).

To understand the movement of methylmercury through the aquatic food web, experiments have been carried out with aquatic animals to quantify methylmercury contributed by each uptake pathway. Jernelov (1972) determined that northern pike (*Esox lucius*) derived 50 percent of its methylmercury body burden from food and 50 percent from water, whereas whitefish (Coregonus clupeaformis) derived only 10 percent from food and 90 percent from water. Huckabee, et al. (1978) concluded that brook trout (Salvelinus fontinalis) acquired approximately half its body burden from food, while Phillips and Buhler (1978) demonstrated that rainbow trout (Salmo gairdneri) accumulated 70 percent from food. Hamilton (1972) concluded from pond experiments with crayfish (Crconectes virilus) on the Wabigoon River that mercury uptake via the food chain was more important than direct uptake from either water or sediment. These studies also showed that the mercury body burden of a given organism is species specific.

The biological studies presented in this section of the report define the present extent of mercury contamination in the Wabigoon/English/Winnipeg River system and examine mercury uptake and movement in some aquatic organisms. Historical data are also reviewed to permit comment on the recovery of the system.

Total mercury analyses were conducted on organisms from three different trophic levels: young-of-the-year (0+) and yearling (1+) northern pike, crayfish, and yearling (1+) yellow perch (Perca flavescens), collected at sites along the Wabigoon/English/Winnipeg River system between 1979 and 1981. Northern pike and yellow perch were chosen because they were abundant and occupied two different trophic levels of an important aquatic food chain. Yellow perch is a secondary consumer with its diet consisting mainly of zooplankton and benthic invertebrates. By contrast, the pike is a large predator. When they reach 5 cm in length, pike eat mainly fish (Scott and Crossman, 1973). Yellow perch data were provided by C. Curry and K. Suns, Limnology and Toxicity Section, Water Resources Branch, Ontario Ministry of the Environment. Suns et al. (1980) demonstrated that young-of-the-year and yearling fish provide good data for determining contaminant uptake as a function of time and location. Unlike adult fish, young fish can be easily aged and, because they are less migratory, their contaminant uptake is confined to a small geographic area. They also represent current rather than historical uptake.

Crayfish are good biological indicators of mercury contamination (Hamilton, 1972; Vermeer, 1972; Armstrong and Hamilton, 1973; Sheffy, 1978) and are an important food source for some predacious fish. The role of crayfish in aquatic communities has been described by Momot, et al. (1978), who stated that crayfish are "polytrophic and a key energy transformer between various trophic links through utilization of all the trophic levels in lakes".

Total mercury analyses were conducted on adult walleye (Stizostedion vitreum) and adult northern pike collected from 1971 to 1982 at three sites in the Wabigoon/English/Winnipeg River system. This study, initiated to address public health concerns, was not funded under the joint federal/provincial agreement. The results, however, are relevant to an understanding of mercury cycling and were provided by B. P. Neary and J. N. Bishop of the Laboratory Services Branch, Ontario Ministry of the Environment, Toronto, Canada.

Finally, an in-situ experiment was conducted in 1978-79 to determine the relative importance of food and water in the bioavailability of mercury and its accumulation in crayfish in the Wabigoon River at the inflow to Clay Lake. This location was of special interest for assessing the effects of the river on biota and remedial measures at Clay Lake.

5.2 METHODS

(a) YOUNG FISH AND CRAYFISH

Young fish and crayfish were sampled at several points between the inflow of the Wabigoon River to Clay Lake, and Eaglenest Lake on the Manitoba border (Figure 5.1). Sites isolated from the contaminated flow were also sampled to determine normal mercury levels. Because water quality in the Wabigoon River between Dryden and Clay Lake is usually too degraded to support fish or crayfish, no samples were collected from that reach. Samples were usually obtained from a restricted area around each site, but certain species (principally pike) were sampled as far as 2 km from the designated sampling site to secure an adequate number of samples.

Northern pike and yellow perch were collected with small mesh nets in shallow (depth <1.25 m), weedy bays. Crayfish were collected with sunken gill nets along shallow (depth <0.5 m), rocky shorelines and baited with fish flesh or commercial dog food. For pike, total length and wet weight were measured, a cleithrum (a bone forming part of the pectoral girdle) and several mid-dorsal scales were taken for age assessment, the fish were stored in plastic "Whirlpac" bags, and frozen on dry ice for transportation to the laboratory. Yellow perch samples were frozen on dry ice immediately after collection. Total length was measured, a scale sample taken, and the fish repackaged into lots of eight for mercury analysis. The length and weight of each crayfish were recorded and a sample of abdominal muscle obtained. Data reported for perch represent the mean values of an eight-fish composite, while those for pike and crayfish are for individual specimens. In 1979, young pike and crayfish were collected from late June to early September. In 1980 and 1981, samples were obtained in mid-August and in September. These differences in exposure times could bias inter-site and inter-year comparisons, particularly between 0+ pike. All samples were analyzed at the Toronto laboratory of the Ontario Ministry of the Environment. Total mercury was determined by flameless atomic absorption, following acid digestion of the samples (Loescher and Neary, 1981).

(b) CRAYFISH CAGING EXPERIMENT

In the first experiment in 1978, crayfish were suspended for 55 days in cages in the Wabigoon River and fed flesh from white sucker fish that contained low mercury levels. A second, more elaborate trial in 1979 used 320 crayfish suspended in cages in the Wabigoon and Eagle Rivers. The crayfish were collected at one of our control sites (Wabigoon Lake) and were divided into four equal groups. Each crayfish was weighed and its length recorded. Each specimen was placed in a 1-litre, numbered compartment of a 40-compartment cage. Cages were constructed from galvanized steel, with the mesh coated with polyamide epoxy resin to prevent mercury adsorption. On June 24, 1979, two groups (160 crayfish) were suspended 1 m below the water surface from an anchored float in the Eagle River, 500 m upstream of Highway 17. Two other groups of crayfish were exposed in similar fashion in the Wabigoon River, 2 km upstream of inflow to Clay Lake. The water depth at each site was about 5 m.

Every 4 days at each location, 80 crayfish were fed about 2 g of white sucker flesh containing an average of 0.13 µg/g of mercury. The other 80 crayfish at each site were fed 2 g of walleye flesh averaging 5.9 µg/g mercury. On August 30, surviving crayfish were weighed and measured. Abdominal muscles were removed from each specimen, placed in a labelled "Whirl-Pak" plastic bag, and frozen. Twenty-eight Wabigoon Lake crayfish were similarly processed on June 24. Total mercury in the muscle samples was determined at the Ministry's Toronto laboratory.

Water samples were collected weekly during the experiment and analyzed for total and methylmercury at the Freshwater Institute, Canada Fisheries and Oceans, Winnipeg. Dissolved oxygen and water temperature were measured in the field, and samples for standard water chemistry analysis were submitted to the Ministry's Thunder Bay laboratory.

(c) ADULT SPORTFISH

Mid-dorsal flesh for mercury analysis was obtained from adult fish collected by the Ontario Ministry of Natural Resources during their routine, mid-summer gill netting program. The length and weight of each fish was recorded. Samples collected in 1971 and 1974 were analyzed at the Freshwater Institute, while those for other years were analyzed by the Toronto laboratory of the Ontario Ministry of the Environment. Collection sites are shown in Figure 5.1.

5.3 RESULTS AND DISCUSSION

(a) ANALYSIS OF DATA FOR YOUNG BIOTA

Tables 5.1-5.4 summarize the average lengths and mercury concentrations for crayfish, perch, and pike collected between 1979 and 1981. Mean mercury levels for all years varied from 0.06 µg/g to 2.2 µg/g for crayfish, 0.01 µg/g to 0.55 µg/g for perch, 0.04 µg/g to 1.0 µg/g for 0+ pike, and from 0.09 µg/g to 1.2 µg/g for 1+ pike. Mercury levels were consistently lowest in perch and highest in crayfish and 1+ pike.

Studies have shown that mercury concentration depends on the length or weight of organism, as well as other factors (Bishop and Neary, 1974; Scott and Armstrong, 1972; Phillips and Buhler, 1978). Many samples may be required to assign statistical significance to the relationship between mercury concentration and any one of these factors (Scott, 1974). In the Wabigoon/English/Winnipeg River system there is normally a relationship between size and mercury concentration in pike from both control sites and contaminated sites (Figure 5.2). Mean mercury concentrations for some sample groups (Figures 5.3 and 5.4) can be compared without making any adjustment for differences in the size. Frequently, however, there is a substantial difference in the mean size of the age class being compared (Figure 5.5). To correct for these differences, we used a geometric regression model, ($y=ax^b$), which yields a linear relationship on a logarithmic scale. Usually, length is the variable that best predicts mercury level (Neary, 1976, Scott, 1974). For sample groups with significantly different mean lengths, data were transformed to the natural logarithm (ln) and the regression model was used to evaluate the mercury/length relationships (see Appendices 5-A, 5-B and 5-C).

The percentage of the mercury/length relationships that were positive (indicating increasing mercury concentrations with size) at contaminated sites was 100 percent for crayfish, 83 percent for 0+ pike, and 60 percent for 1+ pike (Table 5.5). Of the relationships that were positive, 60 percent were statistically significant ($p<.05$) for crayfish, 33 percent were significant for 0+ pike, and 60 percent for 1+ pike. The findings confirmed that size of these organisms must be considered in comparisons between sites and years, even for samples comprising a single age class. No adjustment for length was deemed necessary for comparisons of mercury levels of 1+ perch. Only one of 28 mercury-length relationships was found to be statistically significant.

Analysis of covariance is the normal method of comparing means of different groups, adjusted for a variable such as length. This approach assumes a common slope for the mercury/length relationship of all groups being compared, but this assumption could not be met, in our study, for all inter-site and inter-year comparisons. When no single standardizing procedure could be applied to comparisons of mean mercury concentration, the procedure illustrated in Figure 5.6 was developed to assess the need for a size adjustment and to select the most appropriate adjustment method. The data used in applying the selection procedure are included in Appendix 5-A and 5-B. The inter-site and inter-year comparisons of mercury levels in adult fish were made with concentration values adjusted to a standard length of 50 cm for walleye and 60 cm for pike. Concentrations for these standardized lengths were calculated from mercury-length regression equations in Appendix 5-C.

(b) GEOGRAPHIC TRENDS

1. Young Biota

Geographic trends in mean mercury concentrations are shown in Figure 5.7 for crayfish, in Figure 5.8 for perch, in Figure 5.9 for 0+ pike, and in Figure 5.10 for 1+ pike. Much variation occurred in mercury levels from year to year at different sites. The "relative contamination index" (R.C.I.) shown in the figures was calculated by dividing the mean mercury concentration in biota at each contaminated site by the mean concentration at control sites. Mean R.C.I. values are given in Table 5.6. Three distinct geographic groupings were apparent. The first of these comprised biota from uncontaminated control sites, characterized by mercury concentrations of 0.05 to 0.2 µg/g for crayfish, 0.02 to 0.04 µg/g for yellow perch, 0.05 to 0.07 µg/g for 0+ pike, and 0.1 to 0.15 µg/g for 1+ pike. The second group consisted of sites in the Wabigoon River system from the inlet of Clay Lake to Ball Lake. These sites show the highest contamination, with mercury concentrations ranging from 0.8 to 1.5 µg/g (6 to 13 times background) for crayfish, 0.35 to 0.42 µg/g (12 to 14 times background) for perch, 0.49 to 0.59 µg/g (8 to 10 times background) for 0+ pike, and 0.7 to 1.1 µg/g (5 to 9 times background) for 1+ pike. The final grouping comprised all sites on the English River downstream of Ball Lake and all sites on the Winnipeg River downstream of the English River inflow. Mercury concentrations at these sites were much lower than those for the preceding group, but still above background levels. Concentrations ranged from 0.30 to 0.45 µg/g (2 to 4 times background) for crayfish, 0.04 to 0.09 µg/g (1.3 to 3 times background) for perch, 0.10 to 0.26 µg/g (1.7 to 4 times background) for 0+ pike, and 0.24 to 0.36 µg/g (1.8 to 2.8 times background) for 1+ pike.

Within Clay Lake there was much variation between sites. Mercury levels were usually lowest in biota at the inflow and highest in biota at the outflow. Mercury levels in biota at the Wabigoon River inflow to Ball Lake, located approximately 50 km downstream from Clay Lake, were similar to levels at Clay Lake. In contrast, levels at the outflow of Ball Lake were only a quarter to a half of those at the Wabigoon River inflow. Mercury concentrations in young biota decreased only gradually from this point on, with levels at Eaglenest Lake, 275 km downstream of Dryden, approximately 2 to 8 times background levels. Our crayfish data generally agreed with results reported by Hamilton (1982).

2. Adult Sportfish

Mercury data for 1982 adult walleye and pike are presented in Figures 5.11 and 5.12. Highest mercury concentrations were found in Clay Lake, where mercury in 60 cm pike was about 4 times background, and mercury in 50 cm walleye was 6 times background. Mercury levels in these species in the English River system (Ball and Separation Lakes) were generally 2 to 3 times above normal. The migratory nature of some adult fish is a factor to be considered in assessing data at junctions of major tributaries such as Ball Lake. Here, fish capture data from the Ontario Ministry of Natural Resources show that mercury levels in adult walleye from the northern uncontaminated basin of Ball Lake were similar to levels in fish from the contaminated southern basin. This finding suggests that walleye move freely throughout Ball Lake. Because adult walleye and pike in Ball Lake are exposed, as they migrate, to both contaminated and uncontaminated environments, their mercury levels were lower than those in fish in Separation Lake, the next site downstream.

Mercury concentrations in pike and walleye from Tetu Lake on the Winnipeg River system were near normal. However, fish in Tetu Lake, like those in Ball Lake, may not be continuously exposed to a contaminated environment. Mercury concentrations in 60 cm northern pike averaged 0.60 µg/g (0.53-0.66 µg/g) for Wabigoon, Oak, Maynard, and Sand Lakes. The levels were lower than the average for fish from other uncontaminated lakes in northwestern Ontario (Figure 5.13).

(c) TEMPORAL TRENDS

1. Young Biota

Young biota showed much variation in year-to-year mercury concentrations, both at control and contaminated sites. No consistent pattern emerged (Figures 5.14-5.17). The data suggest, however, that contaminated sites and control sites behave quite differently in the most contaminated reaches of the system, but become similar as distance downstream, and level of contamination, decrease.

Data for crayfish collected annually at Clay Lake since 1970 show a clear exponential decline over a decade (Figure 5.18). The trend suggests that further declines in mercury in biota will occur very slowly in future years.

2. Adult Sportfish

Mercury concentrations in adult walleye (50 cm) and pike (60 cm) for the 1970-82 period are presented in Figures 5.19 and 5.20 for three lakes in the system. Statistics for regressions are found in Appendix 5-C and, as an example, the regressions for northern pike from Clay Lake are plotted in Figure 5-C.1. These figures clearly show that mercury concentrations in adult sportfish have declined over the past decade at all sites, as anticipated following the cessation of large mercury loadings at Dryden.

It is likely that some of the variability in the data in Figure 5.19 comes from sampling more than one walleye stock. In Clay Lake, annual walleye collections have come from different ends of a lake that is capable of holding more than one discrete stock. Scott (1974) noted different age/mercury concentration relationships for walleye and pike obtained from four different parts of Clay Lake. In Tetu Lake (Figure 5.20) the atypical trend for 1974-76 northern pike may also be the result of sampling different stocks.

Growth rate may affect the continuity of the temporal trend for a particular species. For example, between 1972 and 1976, there was a significant increase in growth rate in Clay Lake walleye possibly because of changes in the quality of effluent discharged at Dryden (D. P. Scott, Freshwater Institute, Winnipeg, Canada). This change in growth rate could change the mercury/length relationship for Clay Lake, thus affecting the rate of decrease of mercury concentrations in adult walleye.

(d) MERCURY LEVELS IN YOUNG BIOTA

1. Ranking Young Biota by Mercury Concentration

An assessment of the relative contamination of crayfish, perch, 0+pike, and 1+pike is summarized in Table 5.7. At contaminated sites, the usual ranking by mercury concentration was crayfish > 1+pike > 0+pike > perch. At control sites, the most frequent order was 1+pike > crayfish > 0+pike > perch. The consistency of the ranking 0+pike > perch at all sites, and 1+pike > crayfish at control sites, suggests that for comparison between organsims, time of exposure is not critical. Rather, the ranking reflects magnification up the food chain (biomagnification).

In contrast to free-swimming fish, crayfish are closely associated with the sediments where the highest methylmercury levels would be expected. Moreover, crayfish feed on detritus which might, if contaminated, lead to additional mercury uptake. As the age of the "standard" crayfish (7.1 cm) is probably 2 to 3 years, (W. T. Momot, Lakehead University, Thunder Bay, pers. comm.), it may have been subjected to a longer period of exposure than free-swimming young fish. The tendency for crayfish to have lower mercury levels than 1+ pike at control sites suggests that uptake pathways related to sediments may be of less importance than food chain magnification at these sites.

2. Mercury Relationships Between Organisms at Different Trophic Levels

Similarities in geographic trends suggest the existence of relationships between organisms from different trophic levels. Regressions using standardized samples for various biota are shown in Figures 5.21 to 5.25. Strong relationships were found between mercury levels in different organisms, although the biota being compared occupied different ecological niches where feeding habits, size and period of exposure all varied. The percentage of the total mercury body burden that is in the methyl form probably differs between species. These results suggest that similar environmental factors control the rates of total and methylmercury accumulation. Each of the sampling sites can be considered a similar ecosystem at a different degree of contamination.

(e) SOURCE OF MERCURY IN CAGED CRAYFISH

The first crayfish exposure experiment in 1978 showed that crayfish fed uncontaminated food increased their mercury level from 0.13 μg/g to 0.32 μg/g after 55 days in the Wabigoon River. However, the design of the 1978 trial did not permit evaluation of the relative importance of food and water as the source of mercury.

The data from the 1979 caging experiment are summarized in Table 5.8. Mean mercury levels for each group were derived from geometric regressions of mercury concentrations on length, at a standardized length of 7.3 cm. At both test sites, mercury in crayfish fed on contaminated walleye flesh was many times higher than mercury in crayfish fed on uncontaminated sucker flesh. Mercury concentrations were similar at each site for crayfish on the same diet, whether high or low in mercury. Other than a more rapid weight gain for Wabigoon crayfish compared to Eagle River crayfish, no other significant differences in length or weight could be detected (Table 5.9).

Water quality data for the two sites (Table 5.10) show that both total and methylmercury concentrations in water were higher in the Wabigoon River than the Eagle River. The Wabigoon River was slightly more acidic than the Eagle, and had less dissolved oxygen.

In this experiment, food and water were the only sources of mercury for the crayfish. Our data clearly show that food was by far the most important of these two sources. Little methylmercury was absorbed by crayfish from water at either site, despite the large difference in mercury levels in water at the two locations.

Our findings generally agreed with those reported by Hamilton (1972). Both studies, however, revealed significant accumulation of mercury by crayfish even when fed "uncontaminated" food containing about 0.1 μg/g of mercury. This finding suggests that the uncontaminated food contained much more mercury than food previously consumed by the crayfish in their natural habitat.

(f) BIOLOGICAL INDICATORS OF MERCURY CONTAMINATION

Due to their migratory and age characteristics, adult sportfish are not "ideal" biological indicators of mercury contamination. An ideal indicator should provide data which are directly related to human health, show rapid response to environmental changes, and provide a high degree of confidence (robustness) that the effect was due to the environmental changes being investigated. Many biological indicators available in natural systems do not meet these criteria.

Adult fish, because of their extended exposure periods, are better buffered from the effects of short-term environmental changes than young fish. This buffering is evident when fluctuations in mercury in standardized adult fish are compared with fluctuations in young biota at control sites, where there is no net change in the mercury supply with time. The mercury concentration in 60 cm adult pike (approximately 5 years old) in this situation never changed by more than 23 percent (Table 5.11) while yearly fluctuations in 16 cm pike (a few months old) sometimes exceeded 300 percent. The same would likely apply to contaminated systems provided that decreases in methylmercury were slow enough to allow adult fish to equilibrate with their environment. While adult fish are less responsive than young biota, they are clearly more relevant to human health, since movement of methylmercury into man is by way of consumption of contaminated adult fish.

Young fish are more restricted in their movements, so their contaminant levels better represent local conditions. This feature enhances their use when sampling near large inflows which have no natural barriers to fish movements. Furthermore, as their contaminant uptake is more rapid because of their faster growth rate, they are very responsive to environmental changes. However, this responsiveness makes them less robust indicators.

Crayfish are intermediate between adult fish and young fish in time of exposure, and are similar to young fish in movement. Crayfish also live in close contact with sediment, which, in many parts of the river system, is the major current source of mercury. Crayfish are less subject to the limitations that apply to adult fish and young fish, and offer the best compromise of responsiveness and robustness. Although crayfish lack direct relevance to human health, a relationship between mercury levels in crayfish and young pike can be established (Figure 5.23). It is also possible to establish relationships between crayfish and adult fish.

Of the four groups of young organisms considered, young pike appear to be least suitable as indicator organisms. Although widely distributed along the system, pike are not as abundant as crayfish and perch, are more solitary in their habits, and generally inhabit weedy littoral areas that are difficult to sample effectively. Furthermore, young pike are not always found in the same location from year to year, and may display large variations in size within an age group. More time and effort are required to secure adequate samples of young pike than are required for crayfish and perch. Yellow perch is an abundant, schooling species which shows less variation in growth rate and can be conveniently segregated into age groups. By pooling several fish to form one sample for analysis, estimates of average mercury levels are more robust.

The choice of an indicator organism depends on the specific purposes of the study. In the Wabigoon/English River system, standardized samples of adult walleye and pike provide the most precise data for temporal trends as well as information on appropriate consumption limits. The validity of the data generated is increased if sampling is designed to ensure that the same discrete population is sub-sampled regularly. Data for adult biota can also be used to determine spatial trends in mercury contamination, provided that the population range is suitably restricted to the sites being compared. This requirement is probably not met at Ball and Tetu Lakes, where fish can move easily between clean and contaminated systems. Younger organisms, because of their restricted habitat, are particularly useful in delineating local effects and are very responsive to environmental changes. Young organisms can also provide rapid feedback on the effectiveness of amelioration measures. Some amelioration measures could be evaluated by small-scale tests or pilot projects.

5.4 CONCLUSIONS

1. Mercury concentrations in walleye (Stizostedion vitreum), northern pike (Esox lucius), yellow perch (Perca flavescens) and crayfish (Orconectes virilis) in the Wabigoon/English/Winnipeg River system downstream of Dryden were above background levels. The most contaminated biota were found in Clay Lake. In 1982, total mercury concentrations in adult walleye (50 cm) and northern pike (60 cm) from Clay Lake were 3.8 µg/g and 2.4 µg/g, respectively, well above background levels. Elevated mercury concentrations were also found in yearling yellow perch and crayfish in the Wabigoon system. Less contamination was recorded in biota in the English River system. Standard 50-cm walleye from Ball and Separation Lakes in 1982 contained 1.4 µg/g and 2.1 µg/g mercury, respectively. Mercury concentrations in 60-cm pike from these two lakes were 1.4 and 1.6 µg/g, respectively. These concentrations exceeded background levels by a factor of two or more. Mercury levels in young pike, yellow perch, and crayfish from the outflow of Ball Lake were about two to three times higher than normal levels.

   Biota in the Winnipeg River system that are influenced by English River inflows had mercury concentrations slightly higher than control values. Geographical trends were similar for mercury concentrations in all biota collected at the same time. Mercury in adult walleye and pike from the contaminated Winnipeg River system were similar to those from many other lakes in northwestern Ontario remote from known sources of mercury.

2. Mercury concentrations in adult walleye and pike have declined substantially since 1971 at all sites in the system studied. The rate of improvement in these organisms may be slower in the future than the past: young biota studies suggest slow current rates of change.

3. Statistically significant relationships were found between mercury concentrations in crayfish, young pike, and yellow perch, despite differences in feeding habits, metabolism, habitat, and accumulation pathways. These relationships suggest that

similar environmental factors control the rate of total and methylmercury accumulation by these organisms. Each of the biota sampling sites can be considered a similar ecosystem at a different degree of contamination.

4. Crayfish exposed to different aquatic environments and fed different diets accumulated mercury primarily through contaminated food. Variations in the concentrations of mercury in water had much less effect than the concentrations in food.

5. Young perch and crayfish were good biological indicators of mercury contamination, and were much easier to collect than larger sportfish.

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TABLE 5.1. Total mercury concentrations and lengths of crayfish collected from Wabigoon/English/Winnipeg River System, 1979-81.

Year		Total Mercury (µg/g)			Total Length (cm)		
	N[a]	Mean	S[b]	Range	Mean	S[b]	Range
1979 Wabigoon Lake	28	.16	.10	.03-.51	7.2	.52	6.1-8.1
Clay Lake, Eastern Basin	20	2.2	.66	1.3-3.5	7.2	.45	6.4-8.2
Wabigoon River, Inflow to Ball Lake	21	.80	.20	.42-1.2	6.8	.92	4.2-8.5
English River, Inflow to Ball Lake	30	.25	.80	.09-.49	6.8	.71	5.5-8.2
English River, Outflow to Ball Lake	30	.68	.36	.23-1.5	7.2	.88	5.1-8.8
Sand Lake	14	.26	.11	.10-.52	7.9	.82	7.1-9.8
Eaglenest Lake	18	.43	.12	.24-.68	7.0	.64	5.7-7.9
1980 Wabigoon Lake	30	.09	.04	.01-.17	7.6	.66	6.2-8.7
Eagle Lake/Eagle River	31	.07	.03	.03-.13	7.3	.67	5.9-9.0
Wabigoon River, Inflow to Clay Lake	30	.79	.26	.29-1.4	7.2	.66	5.9-8.3
Wabigoon River, Inflow to Ball Lake	29	1.7	.49	.74-2.7	8.0	.59	6.7-9.3
English River, Inflow to Ball Lake	17	.15	.06	.08-.27	7.1	.54	5.9-8.0
English River, Outflow to Ball Lake	18	.42	.20	.17-.81	7.3	.93	6.2-9.5
Umfreville Lake	4	.25	.08	.19-.37	6.0	.46	5.4-6.4
Roughrock Lake	11	.16	.06	.07-.26	7.1	.66	5.7-8.1
Cygnet Lake	18	.06	.02	.03-.11	6.9	.59	5.9-8.6
Eaglenest Lake	26	.21	.10	.08-.49	7.4	.71	5.7-8.7
1981 Wabigoon Lake	4	.07	.03	.03-.09	7.3	.56	6.6-8.0
Eagle Lake/Eagle River	6	.06	.05	.03-.09	7.2	.32	6.7-7.5
Wabigoon River, Inflow to Clay Lake	13	.76	.20	.05-1.3	6.6	1.5	3.2-8.2
Clay Lake, Eastern Basin	19	.96	.34	.36-1.6	6.1	1.1	4.0-7.7
Wabigoon River, Outflow to Clay Lake	15	.75	.25	.36-1.2	6.8	.46	6.0-7.6
Wabigoon River, Inflow to Ball Lake	40	.91	.25	.38-1.6	7.6	.63	6.1-8.7
English River, Inflow to Ball Lake	42	.12	.06	.03-.30	7.3	.65	5.6-8.6
English River, Outflow to Ball Lake	40	.48	.23	.13-1.10	7.0	.70	5.7-8.4

[a] Number of samples.

[b] Standard deviation of mean.

TABLE 5.2. Total mercury concentrations and lengths of 1+ yellow perch collected from Wabigoon/English/Winnipeg River System, 1979-81.

Year		Total Mercury (μg/g)				Total Length (cm)		
		N[a]	Mean	S[b]	Range	Mean	S[b]	Range
1979	Wabigoon Lake	10	.03	.01	.02-.03	5.2	.14	5.0-5.5
	Wabigoon River, Inflow to Clay Lake	10	.30	.06	.16-.39	5.8	.13	5.6-6.0
	Wabigoon River, Outflow of Clay Lake	8	.38	.06	.31-.49	6.2	.16	6.0-6.4
	Wabigoon River, Inflow to Ball Lake	10	.37	.07	.26-.45	5.1	.07	5.0-5.2
	English River, Inflow to Ball Lake	10	.09	.01	.07-.10	5.4	.11	5.2-5.5
	English River, Outflow to Ball Lake	10	.09	.02	.06-.11	4.9	.26	4.5-5.2
	Lount Lake	10	.02	.01	.01-.02	5.5	.13	5.3-5.7
	Umfreville Lake	10	.07	.01	.06-.08	5.2	.09	5.1-5.4
	Sand Lake	10	.04	.01	.03-.05	4.5	.11	4.3-4.7
	Eaglenest Lake	10	.07	.01	.06-.09	5.2	.09	5.1-5.3
1980	Wabigoon Lake	10	.01	.01	.01-.02	5.6	.18	5.4-6.0
	Eagle Lake/Eagle River	10	.03	.01	.02-.04	5.2	.53	4.6-6.2
	Wabigoon River, Inflow to Clay Lake	8	.18	.05	.12-.26	6.4	.17	6.1-6.7
	Wabigoon River, Outflow to Clay Lake	10	.34	.05	.25-.39	5.8	.15	5.6-6.1
	Wabigoon River, Inflow to Ball Lake	10	.34	.06	.28-.45	5.6	.16	5.3-5.8
	English River, Inflow to Ball Lake	10	.02	.01	.01-.03	5.5	.19	5.3-5.9
	English River, Outflow to Ball Lake	10	.04	.01	.03-.05	5.2	.11	5.0-5.3
1980	Lount Lake	10	.02	.01	.01-.03	4.8	.09	4.7-5.0
	Umfreville Lake	10	.04	.02	.01-.07	4.8	.18	4.5-5.1
	Sand Lake	9	.02	.01	.01-.03	4.8	.09	4.7-5.0
	Eaglenest Lake	10	.04	.01	.02-.06	5.1	.07	5.0-5.2
1981	Wabigoon Lake	8	.02	-	.02-.02	5.6	.11	5.5-5.8
	Eagle Lake/Eagle River	10	.01	.01	.01-.03	5.5	.23	5.0-5.8
	Wabigoon River, Inflow to Clay Lake	10	.55	.07	.44-.66	6.5	.19	6.2-6.8
	Wabigoon River, Outflow to Clay Lake	10	.49	.06	.39-.56	6.0	.18	5.7-6.3
	Wabigoon River, Inflow to Ball Lake	10	.33	.06	.26-.43	5.5	.10	5.4-5.7
	English River, Inflow to Ball Lake	10	.01	-	-	5.1	.13	4.9-5.4
	English River, Outflow from Ball Lake	10	.14	.01	.12-.17	5.2	.21	4.9-5.6

[a] Number of samples.

[b] Standard deviation of mean.

TABLE 5.3. Total mercury concentrations and lengths of 0+ northern pike collected from Wabigoon/English/Winnipeg River System, 1979-81.

Year		Total Mercury (µg/g)			Total Length (cm)		
	N[a]	Mean	S[b]	Range	Mean	S[b]	Range
1979 Wabigoon River, Inflow to Ball Lake	15	.54	.09	.40-.69	13.1	1.2	11.0-15.0
English River, Inflow to Ball Lake (Maynard Lake)	4	.05	.01	.04-.06	10.9	.64	10.0-11.5
Lount Lake	4	.16	.07	.13-.20	12.8	.50	12.0-13.0
Eaglenest Lake	4	.21	.03	.17-.25	13.2	.29	13.0-13.5
1980 Wabigoon Lake	15	.04	.01	.03-.06	15.4	1.9	11.9-18.8
Eagle Lake/Eagle River	26	.05	.03	.01-.13	13.7	2.6	9.1-20.0
Clay Lake, Eastern Basin	10	.22	.11	.08-.43	17.8	1.0	16.3-19.6
Wabigoon River, Outflow to Clay Lake	25	.57	.21	.13-.87	17.3	3.3	11.0-23.0
Wabigoon River, Inflow to Ball Lake	35	.53	.20	.23-1.4	14.6	2.4	10.0-19.3
English River, Inflow to Ball Lake	33	.05	.03	.01-.16	13.8	1.8	8.0-18.3
English River, Outflow of Ball Lake	31	.15	.03	.09-.22	15.0	2.3	10.2-19.0
Lount Lake	26	.17	.04	.07-.24	16.8	2.6	11.5-22.0
Umfreville Lake	34	.10	.02	.06-.18	14.9	2.0	8.9-19.2
Cygnet Lake	34	.06	.03	.03-.14	18.1	2.3	14.0-23.0
Eaglenest Lake	21	.08	.03	.05-.15	17.2	1.9	13.8-20.1
1981 Wabigoon Lake	11	.04	.01	.03-.06	19.8	2.3	15.6-23.8
Eagle Lake/Eagle River	11	.04	.01	.02-.06	15.8	2.3	9.6-18.1
Wabigoon River, Inflow to Clay Lake	12	.73	.20	.40-1.0	22.8	2.8	19.4-27.5
Clay Lake, Eastern Basin	20	.78	.12	.60-1.1	20.0	1.3	17.6-22.3
Wabigoon River, Outflow of Clay Lake	25	1.0	.24	.04-1.5	25.1	3.1	17.7-30.4
Wabigoon River, Inflow to Ball Lake	22	.58	.05	.51-.69	15.7	1.6	12.4-18.2
English River, Inflow to Ball Lake	25	.04	.01	.02-.06	16.8	1.3	13.4-18.7
English River, Outflow of Ball Lake	29	.21	.05	.12-.30	16.0	2.5	9.2-21.3

[a] Number of samples.

[b] Standard deviation of mean.

TABLE 5.4. Total mercury concentrations and lengths of 1+ northern pike collected from Wabigoon/English/ Winnipeg River System, 1980-81.

Year		Total Mercury (µg/g)				Total Length (cm)		
		N[a]	Mean	S[b]	Range	Mean	S[b]	Range
1980	Wabigoon Lake	11	.10	.02	.06-.12	22.5	2.9	19.5-38.0
	Eagle Lake/Eagle River	3	.07	.01	.06-.08	23.9	1.8	22.7-26.0
	Wabigoon River, Inflow to Clay Lake	17	.52	.08	.31-.64	24.5	2.0	18.9-27.9
	Clay Lake, Eastern Basin	35	.77	.10	.60-.98	24.0	2.1	21.0-28.3
	Wabigoon River, Outflow of Clay Lake	4	.89	.10	.76-.99	24.4	1.1	23.5-25.6
	Wabigoon River, Inflow to Ball Lake	1	1.0			24.7		
	English River, Inflow to Ball Lake	1	.09			17.7		
	English River, Outflow to Ball Lake	1	.30			21.0		
	Lount Lake	1	.24			24.7		
	Umfreville Lake	2	.24	.06	.20-.28	25.6	1.1	24.8-26.3
	Eaglenest Lake	13	.20	.05	.09-.30	26.6	3.6	20.7-31.2
1981	Wabigoon River	3	.06	.04	.02-.10	25.1	3.5	22.2-29.0
	Eagle Lake/Eagle River	1	.04			19.4		
	Wabigoon River, Inflow to Clay Lake	14	.89	.26	.58-1.6	25.7	2.9	21.2-31.5
	Clay Lake, Eastern Basin	1	.75			24.1		
	Wabigoon River, Outflow of Clay Lake	3	1.3	.06	1.2-1.3	28.1	.66	27.4-28.7
	Wabigoon River, Inflow to Ball Lake	11	.65	.11	.46-.82	27.6	3.6	18.5-32.1
	English River, Inflow to Ball Lake	1	.10			26.1		
	English River, Outflow of Ball Lake	3	.34	.05	.28-.38	29.2	2.8	26.9-32.3

[a] Number of samples.

[b] Standard deviation.

TABLE 5.5. Trends in mercury concentration/length regressions for young fish and crayfish.

Organism	Sampling Site	Total Number of Sites with n≥10	Number Showing Increasing Trend	Number Significant at p=.05	Number Showing Decreasing Trend	Number Significant at p=.05
Crayfish	Control	7	7	4	0	-
	Contaminated	15	15	9	0	-
1+ Perch	Control	10[1]	4	0	6	1
	Contaminated	18[1]	8	0	10	0
0+ Pike	Control	9	6	1	3	0
	Contaminated	15	12	4	3	1
1+ Pike	Control	4	1	0	3	1
	Contaminated	8	5	3	3	1

[1] Each perch sample was an 8-fish composite, so all perch data is included.

TABLE 5.6. Relative contamination index[a] of selected biota in the Wabigoon/English River system.[b]

Site	1+ Perch	Crayfish	0+ Pike	1+ Pike	Adult Pike	Adult Walleye	Date
Clay Lake inflow[c]	13.8	11.4		7.0	4.9)	9.0	1979-81
Clay Lake, eastern basin[c]		23.5	10.0	7.2)	4.1)	7.0	1981
				)	)		
Clay Lake outflow[c]	16.2	12.0		11.0)	)		
Wabigoon River inflow[c] to Ball Lake	13.5	15.2	9.3	7.4	2.8	3.5	1979-81
Ball Lake outflow[d]	2.2	2.9	3.0	2.0	1.8	2.5	1981

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[a] $\frac{\text{Concentration in biota at contaminated site}}{\text{Concentration in biota at control site(s)}}$

[b] Mean for 2-3 years data.

[c] Control sites are at Wabigoon and Eagle Lakes.

[d] Control sites are in English River upstream of Ball Lake.

TABLE 5.7. Ranking of young biota by mean mercury concentration.

Sampling Station	Ranking of Organisms by Mean Mercury Concentration (1=highest, 4=lowest)				Observed Frequency of Ordering
	Crayfish	Perch	0+ Pike	1+ Pike	
Control	1	4	3	2	2 of 8 cases (25%)
	2	4	3	1	6 of 8 cases (75%)
Contaminated	1	4	3	2	6 of 8 cases (75%)
	2	4	3	1	2 of 8 cases (25%)
Control	1	-	-	2	3 of 9 cases (33%)
	2	-	-	1	6 of 9 cases (67%)
Contaminated	2	-	-	1	10 of 13 cases (77%)
	1	-	-	2	3 of 13 cases (23%)

TABLE 5.8. Effects of exposure to different environments on mercury levels in caged crayfish, June 24-August 30, 1979.

Mercury levels	Concentrations of total and methylmercury in water and crayfish				
	Eagle River		Wabigoon River		Wabigoon Lake
	Total	Methyl	Total	Methyl	Total
In water (mean for 10 weeks, ng/ℓ)	3	0.2	34	16	
In crayfish (low mercury diet)(μg/g)[a]	1.08 (31)[c]		0.64 (33)		
In crayfish (high mercury diet)(μg/g)[b]	27.3 (27)		26.8 (27)		
In crayfish before experiment (μg/g)					0.15 (28)

[a] Sucker flesh containing 0.13 μg/g Hg.

[b] Walleye flesh containing 5.9 μg/g Hg.

[c] Number of crayfish in sample.

TABLE 5.9 Changes in weight, length, and mercury levels in caged crayfish exposed to different environments, June 24-August 30, 1979.

Diet	Eagle River			Wabigoon River		
	Weight (g)	Length (cm)	Mercury (μg/g)	Weight (g)	Length (cm)	Mercury (μg/g)
Low mercury[a]	+0.36	+0.30	+0.93	+1.10	+0.34	+0.49
High mercury[a]	-0.09	+0.30	+27.1	+0.70	+0.29	+26.6

[a] See Table 5.8.

TABLE 5.10. Total and methylmercury concentrations, temperature, pH, conductivity and dissolved oxygen in water from the Eagle and Wabigoon Rivers, June 27 to August 29, 1979.

Date	Total Mercury (ng/ℓ)	Methylmercury (ng/ℓ)	Temp. (°C)	pH	Conductivity (μmhos/cm)	Diss. Oxygen (mg/ℓ)
WABIGOON RIVER						
Jun 29	36	1.6	21.0	6.8	130	
Jul 4	35	1.8	20.5			
11	45	1.9	24.5	6.8	120	
18	35	2.4	21.5			
25	40	2.7	22.0	7.2	120	
Aug 1	32	1.7	21.0			
9	40	0.9	21.0	6.8	140	
15	26	0.9	18.1			3.0
22	26	1.0	20.6	6.7	130	
29	24	0.8	17.0			
Means	34	1.6	20.7	6.9	128	3.0
EAGLE RIVER						
Jun 27	4	<0.2	17.0	7.4	42	
Jul 4	<5	0.2	21.0	7.5	50	
11	<5	0.2	21.5	7.2	50	
18	5	<0.2	20.5	7.6	45	
25	<5	0.3	22.0	7.7	49	
Aug 1	<5	0.5	20.5	7.6	49	
9	<5	<0.2	19.0	7.2	52	8.6
15	6	0.2	19.5	7.5	45	
22	<5	<0.2	21.0	7.9	50	
29	<5	<0.2	20.0	8.1	65	
Means	3	0.2	20.2	7.6	50	8.6

Note: Detection limits for total and methylmercury are 5 and 0.2 ng/ℓ respectively. Means are calculated using one-half of these detection limits for results reported as <5 ng/ℓ or <0.2 ng/ℓ.

TABLE 5.11. Mercury concentrations (μg/g) in 50 cm walleye and 60 cm northern pike from control lakes.

Lake	Year	50 cm Walleye	60 cm Pike
Sand	1974	0.62	0.60
	1975	0.71	0.65
	1976	0.73	0.53
	1977	0.84	0.62
	1978	0.67	0.60
	1979	0.70	0.57
	1980	0.81	0.55
Oak	1971	0.60	0.56
	1975	0.58	0.59
Eagle	1981	0.26	
	1982	0.29	

APPENDIX 5-A

RELATIONSHIP BETWEEN MERCURY CONCENTRATION AND LENGTH FOR SELECTED ORGANISMS

5-A1. 0+ northern pike
5-A2. 1+ northern pike
5-A3. crayfish

SITE CODE

WA	Wabigoon Lake
ER	Eagle River
S1	Clay Lake inflow
S2	Clay Lake eastern basin
S4	Clay Lake outflow
ER1	English River inflow to Ball Lake
WR1	Wabigoon River inflow to Ball Lake
ERO	English River outflow of Ball Lake
LL	Lount Lake
UVL	Umfreville Lake
ENL	Eaglenest Lake
SL	Sand Lake

STATISTICS CODE

n	Number of samples
r	Correlation coefficient
r^2	Coefficient of determination
SEE	Standard error of the estimate
a	Intercept
b	Regression Coefficient
p	Statistical Significance

APPENDIX 5-A1. Relationship between total mercury concentration and length for 0+ northern pike.

Year	Statistic	WA	ER	S1	S2	S4	ERI	WRI	ERO	LL	UVL	ENL
1979	n						4	16		4		4
	r						.65	.24		.10		.01
	r^2						.42	.06		.01		.40
	SEE						.19	.17		.00		.16
	a						-8.43	-1.81		-.611		-1.34
	b						2.23	.46		-.49		-8.44
	p						.25	.25		.47		.52
1980	n	15	26		10	25	33	35	31	36	34	21
	r	.06	.22		.36	.77	.37	.64	-.48	.30	.28	.41
	r^2	.003	.05		.14	.59	.14	.41	.23	.09	.08	.18
	SEE	.28	.57		.51	.34	.49	.25	.17	.28	.24	.29
	a	-3.52	-4.75		-11.1	-6.24	-6.66	-3.89	-.41	-3.36	-3.62	-5.97
	b	.12	.64		3.30	1.97	1.32	1.21	-.57	.54	.46	1.19
	p	.25	.25		.25	.005	.05	.005	.025	.05	.1	.05
1981	n	11	11	12	20	25	25	22	29			
	r	.05	.79	.40	.41	.41	.17	.06	.02			
	r^2	.003	.62	.16	.17	.17	.03	.004	.0003			
	SEE	.30	.20	.29	.14	.22	.33	.09	.26			
	a	-2.82	-7.03	-3.48	-2.98	-2.34	-5.31	-0.41	-1.65			
	b	-0.12	1.40	1.00	0.91	0.72	0.68	-0.05	0.03			
	p	.88	.004	.20	.07	.04	0.43	.78	.93			

APPENDIX 5-A2. Relationship between total mercury concentration and length for 1+ northern pike.

Year	Statistic	WA	ER	S1	S2	S4	ERI	WRI	ERO	LL	UVL	ENL
1980	n	11	3	17	35	4	1	1	1	1	2	13
	r	.08	.89	.15	-.35	-.03					1	.65
	r^2	.001	.79	.02	.12	.0007					1	.39
	SEE	.22	.09	.18	.12	.14					0	.24
	a	-2.81	-8.08	-1.64	1.36	.10					-20.006	-6.11
	b	0.14	1.71	.31	-.51	-.07					5.73	1.36
	p	.25	.25	.25	.05	.25						.025
1981	n	3	1	14	1	3	1	11	3			
	r	.96		.21		-.14		.72	.47			
	r^2	.91		.04		.02		.52	.22			
	SEE	.34		.27		.06		.13	.20			
	a	-21.2		-1.71		1.15		-3.35	-3.78			
	b	5.64		.48		-.27		.88	.80			
	p	.19		.48		.91		.01	.69			

APPENDIX 5-A3. Relationship between total mercury concentration and length for crayfish.

Year	Statistic	WA	ER	S1	S2	S4	ERI	WRI	ERO	UVL	ENL	SL
1978	n	.20			19							
	r	.84			.81							
	r^2	.70			.65							
	SEE	.32			.27							
	a	-7.90			-2.72							
	b	2.33			1.64							
	p	.005			.005							
1979	n	.28			20		30	21	30		18	14
	r	.19			.48		-.01	.64	.36		.51	.44
	r^2	.03			.23		.0001	.41	.13		.26	.19
	a	-5.08			-3.71		-1.39	-2.35	-3.67		-4.00	-5.41
	b	1.56			2.26		-.03	1.10	1.60		1.60	1.93
	p	.25			.05		.96	.005	.05		.05	.1
1980	n	30	31	30			17	29	18	4	26	
	r	.75	.47	.44			.60	.28	.82	.53	.60	
	r^2	.56	.22	.19			.36	.08	.67	.28	.36	
	SEE	.46	.40	.32			.30	.30	.28	.31	.37	
	a	-14.0	-7.22	-3.66			-7.46	-1.76	-7.37	-5.06	-7.00	
	b	5.60	2.24	1.71			2.81	1.09	3.22	2.03	2.68	
	p	.005	.025	.025			.025	.1	.005	.25	.005	
1981	n	4	6	13	19	15	41	40	40			
	r	.91	.18	.54	.64	.49	.34	.51	.60			
	r^2	.82	.03	.29	.40	.24	.11	.26	.37			
	SEE	.25	.66	.21	.32	.30	.48	.26	.40			
	a	-13.55	-7.69	-1.13	-2.33	-4.76	-5.90	-3.74	-6.44			
	b	5.42	2.39	0.44	1.24	2.31	1.82	1.78	2.88			
	p	.094	.734	.057	.003	.064	.031	.0009	.0004			

APPENDIX 5-B

COMPARISONS OF GEOMETRIC MEAN MERCURY CONCENTRATIONS FOR SELECTED ORGANISMS, WITH MERCURY CONCENTRATIONS ADJUSTED FOR LENGTH

5-B1. 0+ northern pike
5-B2. 1+ northern pike
5-B3. crayfish

SITE CODE

WA	Wabigoon Lake
ER	Eagle River
S1	Clay Lake inflow
S2	Clay Lake eastern basin
S4	Clay Lake outflow
ER1	English River inflow to Ball Lake
WR1	Wabigoon River inflow to Ball Lake
ERO	Ball Lake outflow
LL	Lount Lake
UVL	Umfreville Lake
ENL	Eaglenest Lake
SL	Sand Lake

STATISTICS CODE

ns	Not significant
*	$p<.05$
**	$p<.01$
***	$p<.001$

APPENDIX 5-B1. Comparison of geometric mean mercury concentrations in 0+ northern pike with means adjusted for length for untransformed data.

Site	Year	n	Length Range (cm)	Intercept	Slope	Significance of Regression	Homogeneity of Slope	Unadjusted Geometric Mean Mercury Concentration (µg/g)	Adjusted Mercury Concentration (µg/g)	Pooled Regression Coefficient	Significance of Pooled Regression Coefficient
WA	1980	15	11.9-18.8	.04	.000	ns		.042	.042		
	1981	11	15.6-23.8	.05	-.000	ns		.043	.043		
ER	1980	26	9.1-20.0	.00	.004	ns		.053	.055		
	1981	11	9.6-18.1	-.01	.003	*		.043	.037		
S2	1980	10	16.3-19.6	-.32	.03	ns		.221	.167		
	1981	20	17.6-22.3	.06	.04	ns		.784	.44		
S4	1980	25	11.0-23.0	-.29	.05	***	ns	.567	.733	.0425	***
	1981	25	17.7-30.4	.14	.03	*		1.016	.850		*
ERI	1979	4	10.0-11.5	-.07	.01	ns	ns	.045	.061	.004	*
	1980	33	8.0-18.3	-.02	.005	ns		.046	.050		
	1981	25	13.4-18.7	.007	.002	ns		.036	.028		
WRI	1979	16	11.0-15.0	.28	.02	ns	ns	.536	.579	.029	***
	1980	35	10.0-19.3	-.04	.04	**		.533	.534		
	1981	22	12.4-18.2	.61	-.002	ns		.579	.547		
ERO	1980	31	10.2-19.0	.23	-.006	**	ns	.145	.143	-.0034	ns
	1981	29	9.2-21.3	.23	-.001	ns		.211	.212		
LL	1979	4	12.0-13,0	.20	-.003	ns		.157	.200		
	1980	36	11.5-22.0	.10	.004	ns		.165	.162		
ENL	1979	4	13.0-13.5	.30	-.007	ns	ns	.212	.189		
	1980	21	13.8-30.1	-.02	.006	ns		.079	.082		

APPENDIX 5-B1. Comparison of geometric mean mercury concentrations in 0+ northern pike with mean adjusted for length - for ℓn transformed data.

Site	Year	Intercept	Slope	Significance of Regression	Homogeneity of Slope	Unadjusted Geometric Mean Mercury Concentration (µg/g)	Adjusted Mercury Concentration (µg/g)	Pooled Regression Coefficient	Significance of Pooled Regression Coefficient	Significance of Differences in Total Length for Across Years Comparisons	Geometric Adjusted to Mean Length for Site
WA	1980	-3.52	.12	ns			.041	.041			
	1981	-2.82	-.12	ns			.041	.041			
ER	1980	-4.75	.64	ns			.046	.048			
	1981	-7.03	1.40	**			.041	.038			
S2	1980	-11.1	3.30	ns			.198	.181			
	1981	-2.98	.91	ns			.779	.596			
S4	1980	-6.24	1.97	**	*	.502	.700	1.59	***	***	.76
	1981	-2.34	.72	*			.990	.730			.85
ERI	1979	-8.43	2.23	ns	ns	.044	.063	1.21	**	***	
	1980	-6.66	1.32	*			.040	.044			
	1981	-5.31	.68	ns			.034	.029			
WRI	1979	-1.81	.46	ns	*	.527	.579	.906	***	**	.56
	1980	-3.89	1.21	**			.507	.508			.52
	1981	-.41	-.05	ns			.577	.537			.58
ERO	1980	-.41	-.57	*	ns	ns	.142	.141	-2.76	ns	ns
	1981	-1.65	.03	ns			.204	.207			
LL	1979	-.611	-.492	ns			.156	.139			
	1980	-3.36	.54	ns			.159	.155			
ENL	1979	-1.34	-.08	ns			.210	.194			
	1980	-5.97	1.19	ns			.075	.077			

APPENDIX 5-B2. Comparison of geometric mean mercury concentrations in 1+ northern pike with means adjusted for length for untransformed data.

Site	Year	n	Length Range (cm)	Intercept	Slope	Significance of Regression	Homogeneity of Slope	Unadjusted Geometric Mean Mercury Concentration (μg/g)	Adjusted Mercury Concentration (μg/g)	Pooled Regression Coefficient	Significance of Pooled Regression Coefficient
WA	1980	11	19.5-38.0	.08	.0009	ns		.096	.097		
	1981	3	22.2-24.0	-.23	.01	ns		.057	.056		
ER	1980	3	22.7-26.0	-.05	.005	ns		.070	.070		
	1981	1	19.4					.040			
S1	1980	17	18.9-27.9	.39	.006	ns	ns	.524	.530	.013	ns
	1981	14	21.2-31.5	.46	.02	ns		.888	.880		
S2	1980	35	21.0-28.3	1.17	-.017	*		.774	.790		
S4	1980	4	23.5-25.6	.85	.002	ns	ns	.893	.891	-.001	ns
	1981	3	27.4-28.7	1.59	-.01	ns		1.267	1.269		
ERI	1980	1	17.7					.090			
	1981	1	26.1					.100			
WRI	1980	1	24.7					1.00			
	1981	11	18.5-32.1	.07	.02	*		.645	.642		
ERO	1980	1	21.0					.30			
	1981	3	26.9-32.3	.06	.01	ns		.337			
LL	1980	1	24.7					.240			
UVL	1980	2	24.8-26.3	-1.12	.053			.240			
ENL	1979	17	24.0-35.0	.43	-.001	ns	ns	.397	.392	.004	ns
	1980	13	20.7-31.2	-.03	.009	*		.202	.209		

APPENDIX 5-B2. Comparison at geometric mean mercury concentrations in 1+ northern pike with mean adjusted for length - for ℓn transformed data.

Site	Year	Intercept	Slope	Significance of Regression	Homogeneity of Slope	Unadjusted Geometric Mean Mercury Concentration (µg/g)	Adjusted Mercury Concentration (µg/g)	Pooled Regression Coefficient	Significance of Pooled Regression Coefficient	Significance of Differences in Total Length for Across Years Comparisons	Geometric Adjusted to Mean Length for Site
WA	1980	-2.81	0.14	ns		.095	.095				
	1981	-21.2	5.64	ns		.046	.045				
ER	1980	-8.08	1.71	ns		.070 .040	.067				
S1	1980	-1.64	.31	ns	ns	.516	.520	.408	ns	ns	
	1981	-1.71	.48	ns		.858	.850				.75
S2	1980	1.36	-.51	*		.768	.768				
S4	1980	.10	-.07	ns	ns	.889	.883	-.102	ns	**	
	1981	1.15	-.27	ns		1.266	1.276				
ERI	1979					.09 .10					
WRI	1979					1.00					
	1981	-3.35	.88	*		.636 .30	.634				
ERO	1981	-3.78	.80	ns		.333					
UVL	1980	-20.0	5.73			.237					.21
ENL	1980	-6.11	1.36	*		.194	.204				

APPENDIX 5-B3. Comparison of geometric mean mercury concentrations in abdominal muscle of crayfish with means adjusted for length for untransformed data.

Site	Year	n	Length Range (cm)	Intercept	Slope	Significance of Regression	Homogeneity of Slope	Unadjusted Geometric Mean Mercury Concentration (μg/g)	Adjusted Mercury Concentration (μg/g)	Pooled Regression Coefficient	Significance of Pooled Regression Coefficient
WA	1978	20	4.5-8.5	-.09	.03	***	**	.089	.105	.0295	**
	1979	28	6.1-8.1	-.03	.03	ns		.163	.164		
	1980	30	6.2-8.7	-.19	.04	***		.085	.074		
	1981	4	6.6-8.0	-.23	.04	*		.065	.064		
ER	1980	31	5.9-9.0	-.05	.02	*	ns	.069	.069	.0174	*
	1981	6	6.7-7.5	-.29	.05	ns		.060	.062		
S1	1980	30	5.7-8.3	-.36	.16	*	ns	.788	.771	.0973	*
	1981	13	3.2-8.2	.29	.07	ns		.755	.795		
S2	1978	19	4.0-8.0	-.76	.35	***	ns	1.328	1.460	.3022	***
	1979	20	6.4-8.2	-2.91	.71	*		2.175	1.954		
	1981	19	4.0-7.7	-1.14	.18	**		.963	1.064		
ERI	1979	30	5.5-8.2	.23	.001	ns	ns	.247	.253	.0200	ns
	1980	17	5.9-8.0	-.30	.06	*		.152	.151		
	1981	41	5.6-8.6	-.05	.02	ns		.114	.110		
WRI	1979	21	4.2-8.5	-.05	.13	**	ns	.800	.939	.1840	***
	1980	29	6.7-9.3	-.23	.24	ns		1.715	1.631		
	1981	40	6.1-8.7	-.68	.21	***		.908	.896		
ERO	1979	30	5.1-8.8	-.41	.15	*	ns	.680	.668	.1769	***
	1980	18	6.2-9.5	-.91	.18	***		.421	.390		
	1981	40	5.7-8.4	-.95	.20	***		.482	.504		
ENL	1979	18	5.7-7.9	-.19	.09	ns	ns	.429	.449	.0776	**
	1980	26	5.7-8.7	-.32	.07	**		.213	.200		

APPENDIX 5-B3. Comparison at geometric mean mercury concentrations in abdominal muscle of crayfish with means adjusted for length for ℓn transformed data.

Site	Year	Intercept	Slope	Significance of Regression	Homogeneity of Variance	Homogeneity of Slope	Unadjusted Geometric Mean Mercury Concentration (µg/g)	Adjusted Mercury Concentration (µg/g)	Pooled Regression Coefficient	Significance of Pooled Regression Coefficient	Significance of Differences in Total Length for Across Years Comparisons
WA	1978	-7.90	2.83	**	ns	ns	.078	.104	3.39	***	***
	1979	-5.08	1.56	ns			.138	.136			
	1980	-14.0	5.60	**			.072	.060			
	1981	-13.55	5.42	ns			.060	.059			
ER	1980	-7.22	2.24	*	ns	ns	.063	.063	2.25	*	ns
	1981	-7.69	2.39	ns			.050	.052			
S1	1980	-3.66	1.71	*	ns	ns	.748	.728	.686	*	ns
	1981	-1.13	0.44	ns			.733	.776			
S2	1978	-2.72	1.64	**	ns	ns	1.221	1.363	1.49	***	**
	1979	-3.71	2.26	*			2.075	1.738			
	1981	-2.33	1.24	**			.896	.977			
ERI	1979	-1.39	-.03	ns	ns	ns	.235	.246	1.20	*	**
	1980	-7.46	2.81	*			.142	.141			
	1981	-5.90	1.82	ns			.102	.098			
WRI	1979	-2.35	1.10	**	ns	ns	.771	.893	1.30	***	***
	1980	-1.76	1.09	ns			1.649	1.516			
	1981	-3.74	1.78	***			.869	.858			
ERO	1979	-3.67	1.60	*	ns	ns	.589	.578	2.43	***	ns
	1980	-7.37	3.22	**			.375	.375			
	1981	-6.44	2.88	***			.432	.449			
ENL	1979	-4.00	1.60	*	ns	ns	.411	.446	2.28	***	ns
	1980	-7.00	2.68	**			.194	.183			

APPENDIX 5-C

SUMMARY STATISTICS FOR ADULT WALLEYE AND NORTHERN PIKE WABIGOON/ENGLISH/WINNIPEG RIVER SYSTEM

APPENDIX 5-C1(a). Clay Lake northern pike, 1971-82.

APPENDIX 5-C1(b). Clay Lake walleye, 1970-82.

APPENDIX 5-C2(a). Ball Lake pike, 1971-82.

APPENDIX 5-C2(b). Ball Lake walleye, 1979-82.

APPENDIX 5-C3(a). Separation Lake pike, 1971-82.

APPENDIX 5-C3(b). Separation Lake walleye, 1971-82.

APPENDIX 5-C4(a). Tetu Lake pike, 1974-82.

APPENDIX 5-C4(b). Tetu Lake walleye, 1974-82.

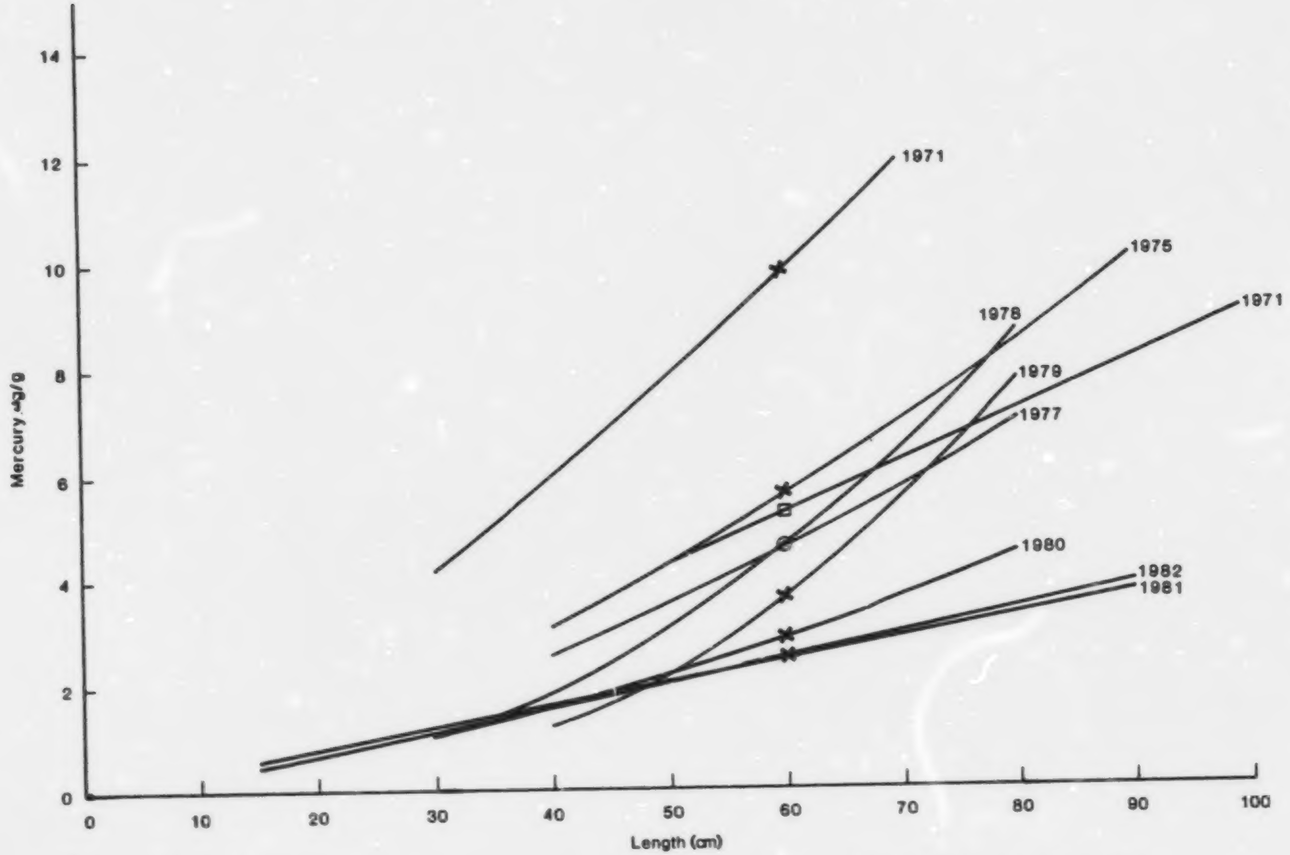

Figure 5-C.1 Regression of total mercury on length for northern pike in Clay Lake, 1971-82.

APPENDIX 5-C1(a) Clay Lake northern pike, 1971-82.

Year	n	Mercury (µg/g)		Length (cm)		Weight (g)		Log (Hg) on Log Length[a]		
		Mean	Range	Mean	Range	Mean	Range	A0	A1	r^2
1971	25	9.09	3.79-14.9	50.8	36.0-62.0	974	312-1870	-2.808	1.264**	0.259
1976	51	5.84	3.60-13.0	65.0	50.1-86.2	1793	879-4423	-2.919	1.131**	0.325
1977	30	4.83	2.20- 8.4	61.3	45.0-70.0	1628	650-2550	-4.145	1.402**	0.252
1978	20	4.67	0.97- 8.5	58.7	37.0-73.5	1411	300-2500	-7.056	2.125**	0.644
1979	24	3.87	0.98- 7.0	60.4	45.0-76.4	1567	500-3500	-9.313	2.621**	0.638
1980	17	2.44	0.85- 5.5	49.2	30.0-73.2	846	125-2400	-4.753	1.432*	0.264
1981	17	2.34	0.63- 5.7	55.7	34.0-87.0	1764	900-2400	-4.462	1.326**	0.524
1982	21	2.32	0.44- 4.7	53.5	16.5-84.0	1096	21-4200	-3.584	1.104**	0.364

[a] $\ln [Hg]_{ppm} = A0 + A1 \times \ln L_{cm}$

[b] * = $p<.01$
** = $p<.05$

APPENDIX 5-C1(b). Clay Lake walleye, 1970-82.

Year	n	Mercury (µg/g)		Length (cm)		Weight (g)		Log (Hg) on Log Length[a]		
		Mean	Range	Mean	Range	Mean	Range	A0	A1	r^2
1970	274	12.1	1.2 -24.0	41.6	22.5-53.0	954	370-1900	-2.969	1.453**	0.235
1971	24	8.71	1.82-14.2	42.6	33.0-50.0	1064	454-1850	-0.481	0.680	0.020
1975	7	5.98	4.60- 8.7	47.2	42.5-53.0	1179	995-1580	-7.264	2.377*	0.463
1976	50	7.83	4.50-12.1	49.8	40.8-59.4	1283	482-2013	-2.349	1.141**	0.253
1977	30	6.97	2.90- 9.9	50.3	42.0-59.0	1321	910-1920	-3.347	1.365**	0.267
1978	7	6.87	3.93-11.2	43.4	29.0-59.0	1019	250-2100	-3.122	1.355**	0.848
1979	51	5.90	3.06- 9.9	47.0	32.7-62.2	1068	340-2220	-3.793	1.463**	0.777
1980	16	8.64	3.67-13.1	55.5	41.3-63.0	1672	752-2150	-8.377	2.654**	0.915
1981	18	6.74	3.30-11.0	56.1	44.6-65.2	1764	900-2400	-11.20	3.290**	0.848
1982	[illegible]0	4.36	1.20-8.70	51.6	28.0-67.5	1605	200-3100	-6.254	1.972**	0.810

[a] $\ln Hg_{ppm} = A0 + [A1 \times \ln L_{cm}]$

[b] * = p<.01
** = p<.05

APPENDIX 5-C2(a). Ball Lake pike, 1971-82.

Year	n	Mercury (µg/g)		Length (cm)		Weight (g)		Log (Hg) on Log Length[a]		
		Mean	Range	Mean	Range	Mean	Range	A0	A1	r^2
1971	20	5.53	1.38-14.9	58.7	48.0-75.0	1517	765-3572	-7.666	2.269*	0.204
1974	32	2.95	0.54-7.95	67.6	50.8-82.6	2314	327-4308	-8.470	2.227*	0.140
1975	42	4.02	0.89-10.7	62.1	43.0-81.6	1585	129-4350	-6.113	1.781**	0.289
1976	49	2.95	0.38-9.40	52.3	29.0-92.5	1146	190-6895	-8.111	2.252**	0.383
1977	27	2.85	0.52-7.50	65.9	48.0-100.	1841	500-8000	-7.733	2.054**	0.381
1978	20	3.14	1.10-5.20	63.8	45.5-84.0	1609	507-3378	-7.787	2.124**	0.473
1979	20	2.13	0.60-5.43	67.8	50.0-84.0	1885	737-3856	-3.938	1.076	0.052
1980	20	2.50	0.88-4.70	70.4	54.0-98.0	2178	900-7800	-7.187	1.878*	0.183
1981	10	1.52	0.36-7.00	58.8	44.0-90.0	1676	563-4050	-14.59	3.578**	0.745
1982	20	1.65	0.47-3.80	60.9	31.0-97.0	1785	200-5600	-7.190	1.833**	0.649

[a] $\ln Hg_{ppm} = A0 + [A1 \times \ln L_{cm}]$

[b] * = $p<.01$

** = $p<.05$

APPENDIX 5-C2(b). Ball Lake walleye, 1979-82.

Year	n	Mercury (µg/g)		Length (cm)		Weight (g)		Log (Hg) on Log Length[a]		
		Mean	Range	Mean	Range	Mean	Range	A0	A1	r^2
1971	20	2.88	0.80-6.22	41.1	31.0-50.0	921	340-1701	-2.040	0.810	0.045
1974	50	2.45	0.94-4.42	46.0	34.3-58.4	1189	397-2466	-2.040	0.810	0.045
1975	58	1.58	0.41-4.26	44.3	22.5-61.5	936	85-2875	-2.237	0.710	0.047
1976	48	2.23	0.28-4.70	36.6	27.5-48.0	578	200-1400	-9.889	2.964**	0.346
1977	30	1.52	0.67-3.10	44.2	35.0-59.0	638	200-1900	-2.124	.753*	.214
1978	20	2.13	0.71-3.50	42.9	23.5-58.0	901	114-1800	-2.080	0.753*	0.214
1979	20	1.92	0.94-3.60	45.8	26.0-62.5	1055	113-2268	-2.498	0.828*	0.361
1980	20	1.70	0.96-2.45	47.9	37.0-58.0	1125	450-1800	-3.169	0.963*	0.144
1981	20	1.17	0.25-2.60	42.0	25.0-57.0	934	113-1913	-6.714	1.841**	0.558
1982	20	1.23	0.50-2.10	44.2	30.0-59.0	1045	300-2200	-5.965	1.638**	0.657

[a] $\ln Hg_{ppm} = A0 + [A1 \times \ln L_{cm}]$

[b] * = $p<.01$

** = $p<.05$

APPENDIX 5-C3(a). Separation Lake pike, 1971-82.

Year	n	Mercury (μg/g)		Length (cm)		Weight (g)		Log (Hg) on Log Length[a]		
		Mean	Range	Mean	Range	Mean	Range	AO	A1	r^2
1971	20	5.09	1.42-14.8	56.9	42.0-76.0	1474	510-4110	-3.925	1.348**	0.1[illegible]
1974	50	2.96	0.81-6.52	62.1	41.9-80.0	1794	510-3968	-3.194	1.005	0.066
1975	29	2.84	0.91-5.89	58.5	36.6-81.3	1283	400-3820	-6.276	1.800**	0.478
1976	49	2.95	0.38-9.40	52.3	29.0-92.5	1146	190-6895	-8.095	2.255**	0.383
1977	24	2.47	0.75-5.00	59.1	48.5-73.0	1172	405-2270	-6.636	1.852**	0.225
1979	20	1.91	0.83-4.53	57.0	43.0-78.0	1145	397-3176	-5.809	1.600**	0.371
1980	20	2.10	0.64-4.16	61.5	31.0-88.0	1643	300-5400			
1[illegible]	20	1.42	0.20-3.60	57.0	27.5-87.5	1783	113-6300			
1982	22	2.25	0.50-4.30	69.7	37.5-98.0	2505	300-6500	-6.864	1.814**	0.683

[a] $\ln Hg_{ppm} = AO + [A1 \times \ln L_{cm}]$

[b] * = p<.01

** = p<.05

APPENDIX 5-C3(b). Separation Lake walleye, 1971-82.

Year	n	Mercury (µg/g)		Length (cm)		Weight (g)		Log (Hg) on Log Length[a]		
		Mean	Range	Mean	Range	Mean	Range	A0	A1	r^2
1971	20	2.96	1.79-4.53	40.7	30.0-48.0	829	284-1361	-1.832	0.781	0.128
1974	50	2.77	0.76-4.51	44.4	36.8-58.4	1019	652-2183	-7.332	2.187**	0.339
1975	51	2.99	1.18-4.58	44.5	24.5-55.0	885	160-1550	-5.453	1.743**	0.578
1976	48	2.23	0.28-4.70	36.6	27.5-48.0	578	200-1400	-4.093	1.312**	0.426
1977	30	2.82	0.79-8.60	43.2	34.5-60.0	764	167-2152	-1.919	0.771	0.065
1979	20	2.61	1.48-4.98	45.6	38.5-60.0	958	567-2041	-4.328	1.395**	0.294
1980	19	1.95	0.80-3.24	44.7	32.0-62.0	987	300-2100			
1981	20	1.22	0.54-4.50	38.3	22.5-60.0	1001	225-2475			
1982	23	1.89	0.71-3.10	44.0	20.0-85.0	1013	100-3000	-4.100	1.261**	0.759

[a] $\ln Hg_{ppm} = A0 + [A1 \times \ln L_{cm}]$

[b] * = $p<.01$

** = $p<.05$

APPENDIX 5-C4(a). Tetu Lake pike, 1974-82.

Year	n	Mercury (μg/g)		Length (cm)		Weight (g)		Log (Hg) on Log Length[a]		
		Mean	Range	Mean	Range	Mean	Range	A0	A1	r^2
1974	48	1.74	0.22-6.51	55.9	39.4-85.1	1635	482-6208	-15.34	3.868**	0.564
1975	32	2.87	0.99-10.3	63.5	46.0-97.3	1919	530-7500	-7.823	2.133**	0.508
1976	47	2.23	0.92-6.20	50.9	39.5-79.0	995	420-3750	-8.076	2.241**	0.603
1977	30	1.93	0.24-5.80	56.5	36.0-79.0	1132	298-3178	-12.43	3.249**	0.733
1978	20	1.56	0.63-4.00	59.4	52.0-71.0	1202	825-2028	-9.568	2.460*	0.179
1979	20	1.32	0.66-2.05	58.9	51.0-74.0	1236	794-2495	-0.159	0.098	0.001
1980	19	1.08	0.61-2.59	66.6	58.0-77.0	1805	900-3000	0.029	-0.003	0.000
1981	19	0.93	0.26-2.30	66.2	42.5-105.	2214	450-7425	-7.270	1.709**	0.293
1982	20	1.17	0.54-2.20	66.4	52.0-101.	1810	700-6500	-5.156	1.269*	0.197

[a] $\ln Hg_{ppm} = A0 + [A1 \times \ln L_{cm}]$

[b] * = $p<.01$

** = $p<.05$

APPENDIX 5-C4(b). Tetu Lake walleye, 1974-82.

Year	n	Mercury (µg/g)		Length (cm)		Weight (g)		Log (Hg) on Log Length[a]		
		Mean	Range	Mean	Range	Mean	Range	A0	A1	r^2
1974	50	1.45	0.40-2.70	44.2	35.6-55.9	1096	510-2013	-7.108	1.955**	0.267
1975	50	1.86	0.58-3.98	46.2	20.5-66.5	1045	80-3050	-5.456	1.571**	0.629
1976	48	1.65	0.65-3.90	37.3	20.5-51.0	632	90-1550	-4.540	1.381**	0.498
1977	30	1.43	0.48-6.00	40.6	21.0-76.0	751	58-4086	-4.839	1.361**	0.391
1978	20	1.07	0.33-2.30	38.8	21.0-64.0	672	57-2508	-4.628	1.261**	0.463
1979	20	1.07	0.36-2.23	40.4	32.0-60.0	651	284-1680	-4.550	1.230*	0.192
1980	19	0.80	0.43-1.13	47.7	41.0-58.0	1037	700-1800	-8.954	2.249**	0.394
1981	20	0.77	0.26-1.50	44.9	30.0-57.5	996	225-2250	-8.300	2.092**	0.693
1982	20	0.75	0.32-2.30	38.3	23.0-56.0	730	100-1900	-5.656	1.452**	0.758

[a] $\ln Hg_{ppm} = A0 + [A1 \times \ln L_{cm}]$

[b] * = p<.01
** = p<.05

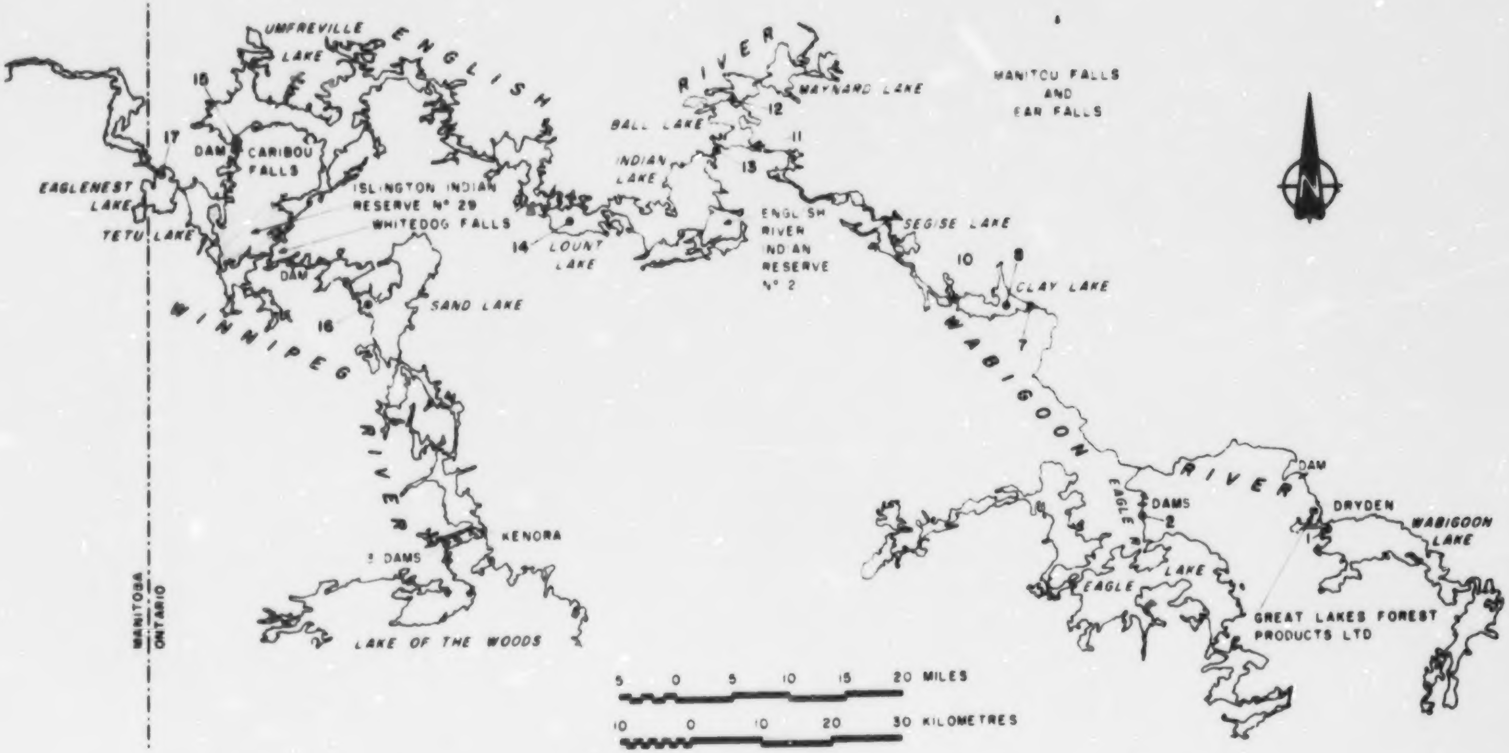
UMFREVILLE LAKE
ENGLISH
RIVER
MAYNARD LAKE
MANITOU FALLS AND EAR FALLS
N
15
17
DAM
CARIBOU FALLS
EAGLENEST LAKE
TETU LAKE
ISLINGTON INDIAN RESERVE Nº 29
WHITEDOG FALLS
DAM
BALL LAKE
12
11
INDIAN LAKE
13
ENGLISH RIVER INDIAN RESERVE Nº 2
14
LOUNT LAKE
SEGISE LAKE
10
8
CLAY LAKE
7
SAND LAKE
16
WINNIPEG
RIVER
WABIGOON
RIVER
KENORA
2 DAMS
LAKE OF THE WOODS
MANITOBA
ONTARIO
EAGLE
DAMS
2
EAGLE LAKE
DAM
DRYDEN
WABIGOON LAKE
1
GREAT LAKES FOREST PRODUCTS LTD
5 0 5 10 15 20 MILES
10 0 10 20 30 KILOMETRES

Figure 5.1 Biota sampling sites on the Wabigoon/English/Winnipeg River system.

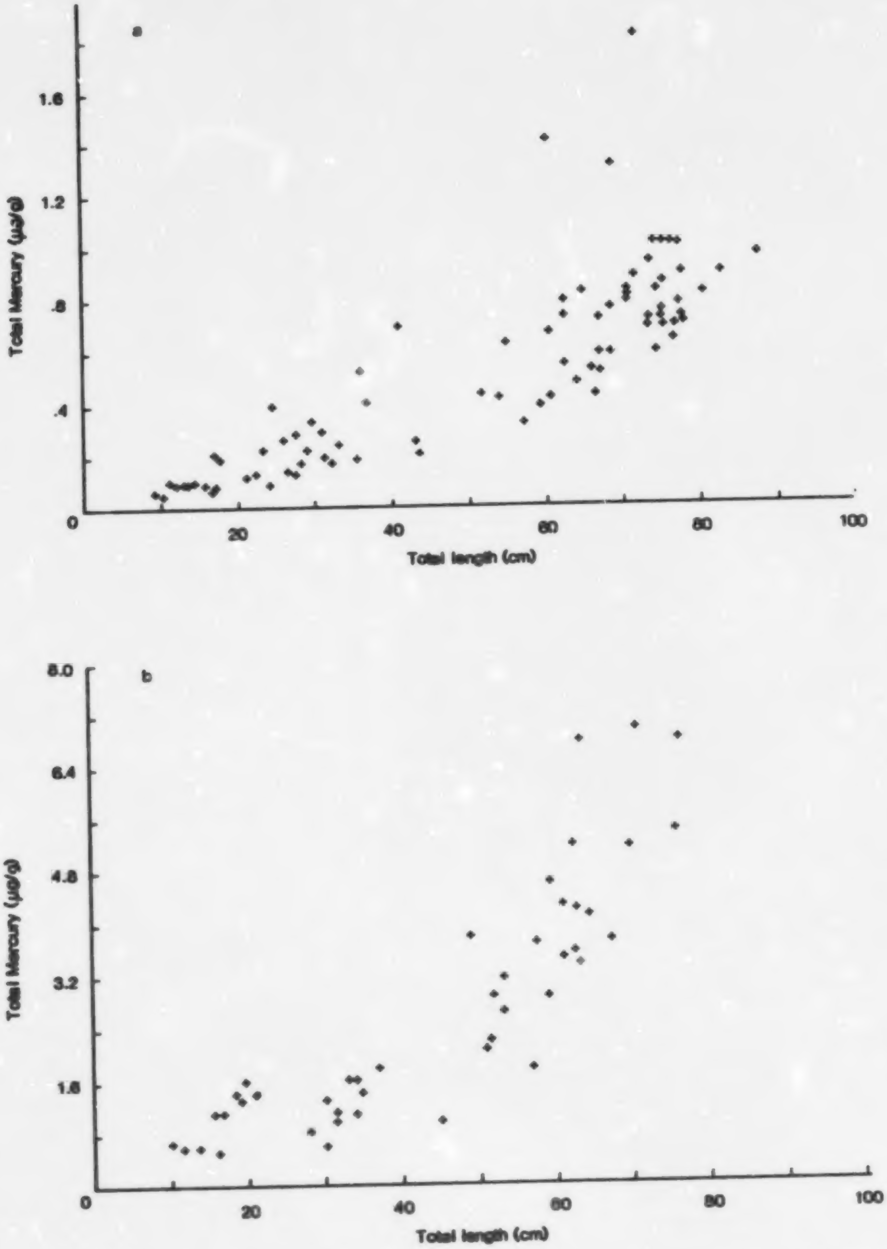

Figure 5.2 Relationship between mercury concentration and total length for northern pike from a non-contaminated site and a contaminated site (a) Wabigoon Lake - 1976, (b) Clay Lake - 1980.

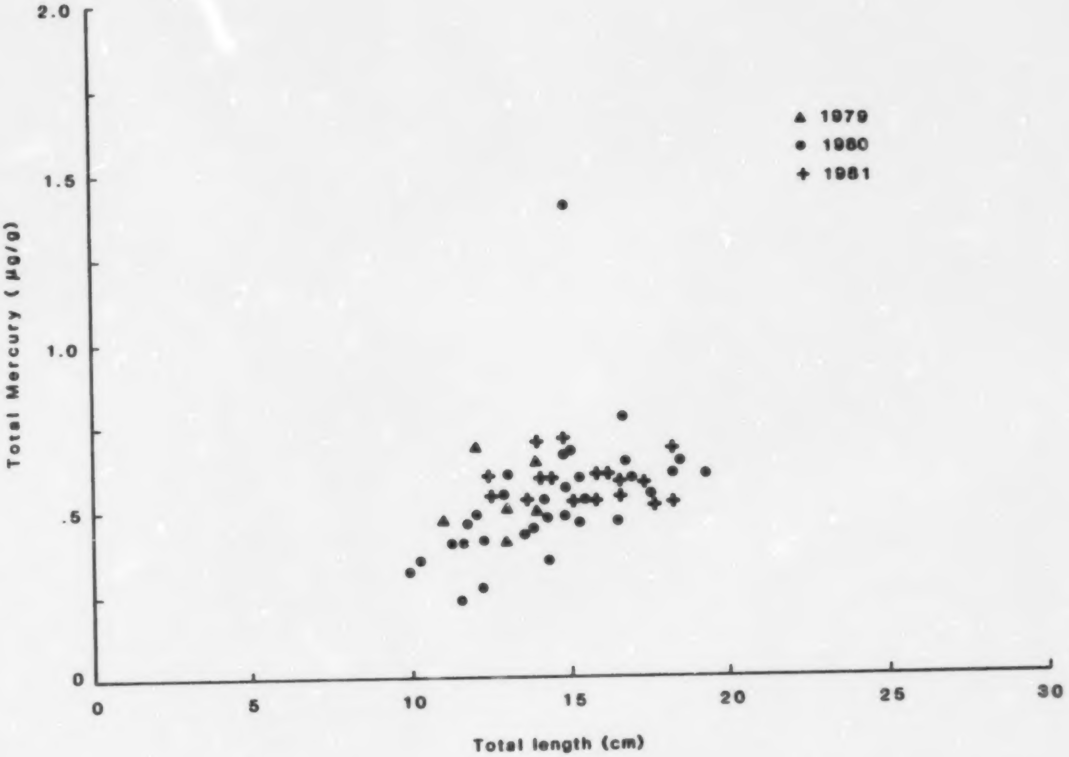

Figure 5.3 Total mercury concentrations for 0+ northern pike from the Wabigoon River inflow to Ball Lake: 1979, 1980, and 1981.

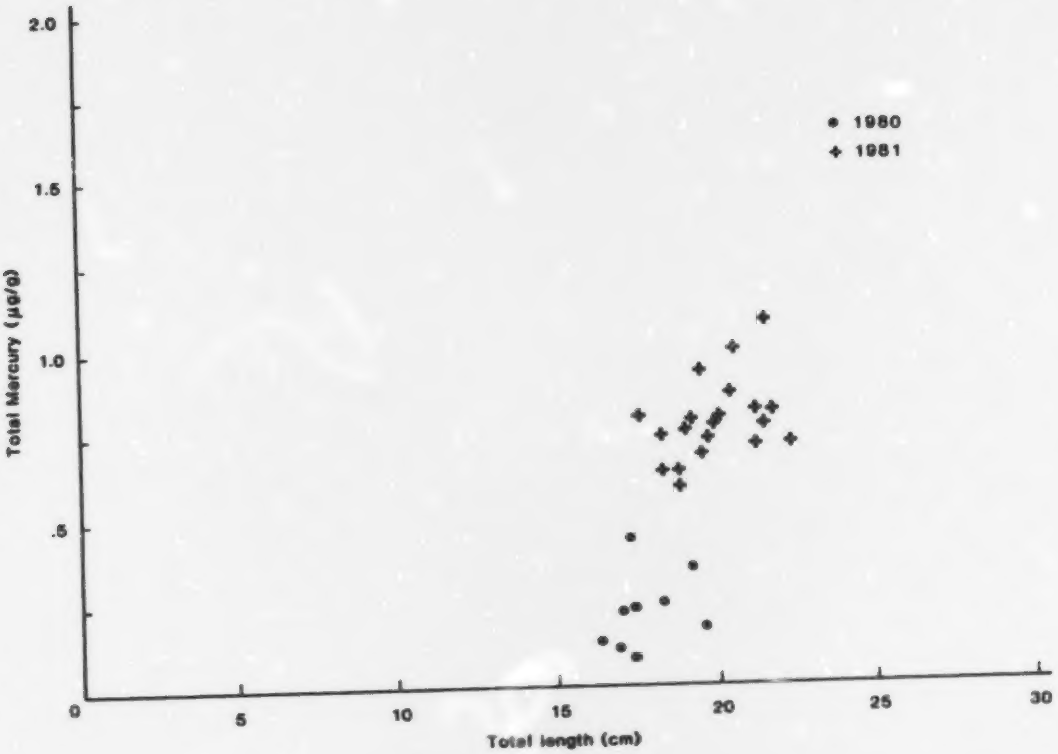

Figure 5.4 Total mercury concentrations for 0+ northern pike from the eastern basin of Clay Lake: 1980 and 1981

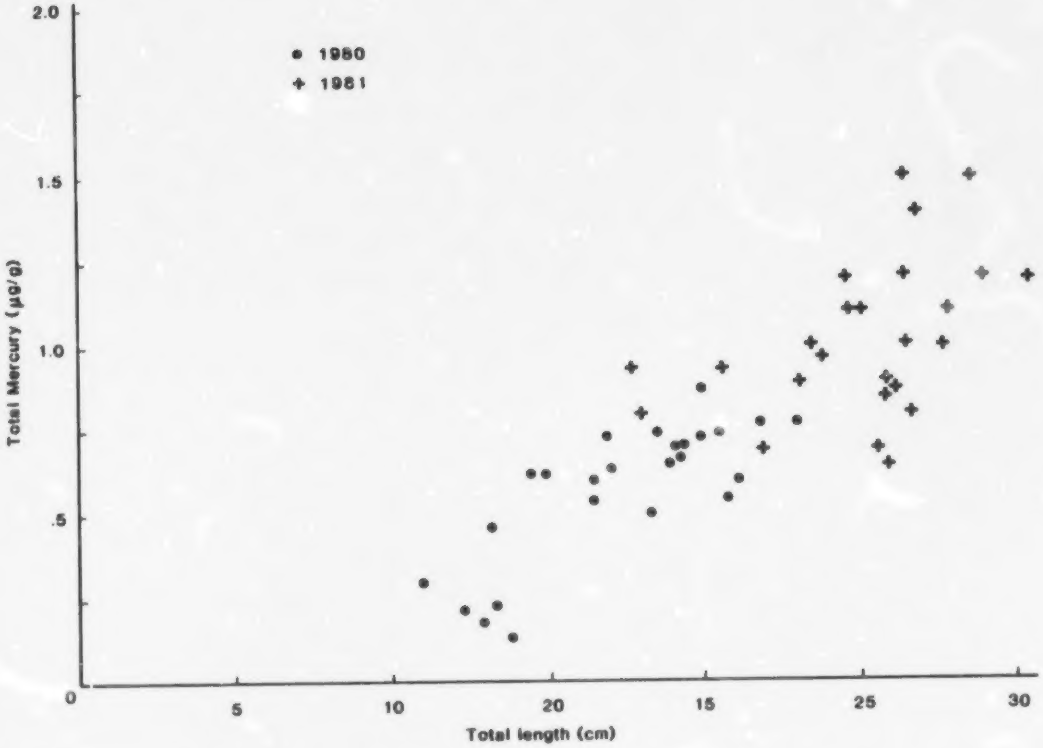

Figure 5.5 Total mercury concentrations for 0+northern pike from Clay Lake outflow: 1980 and 1981.

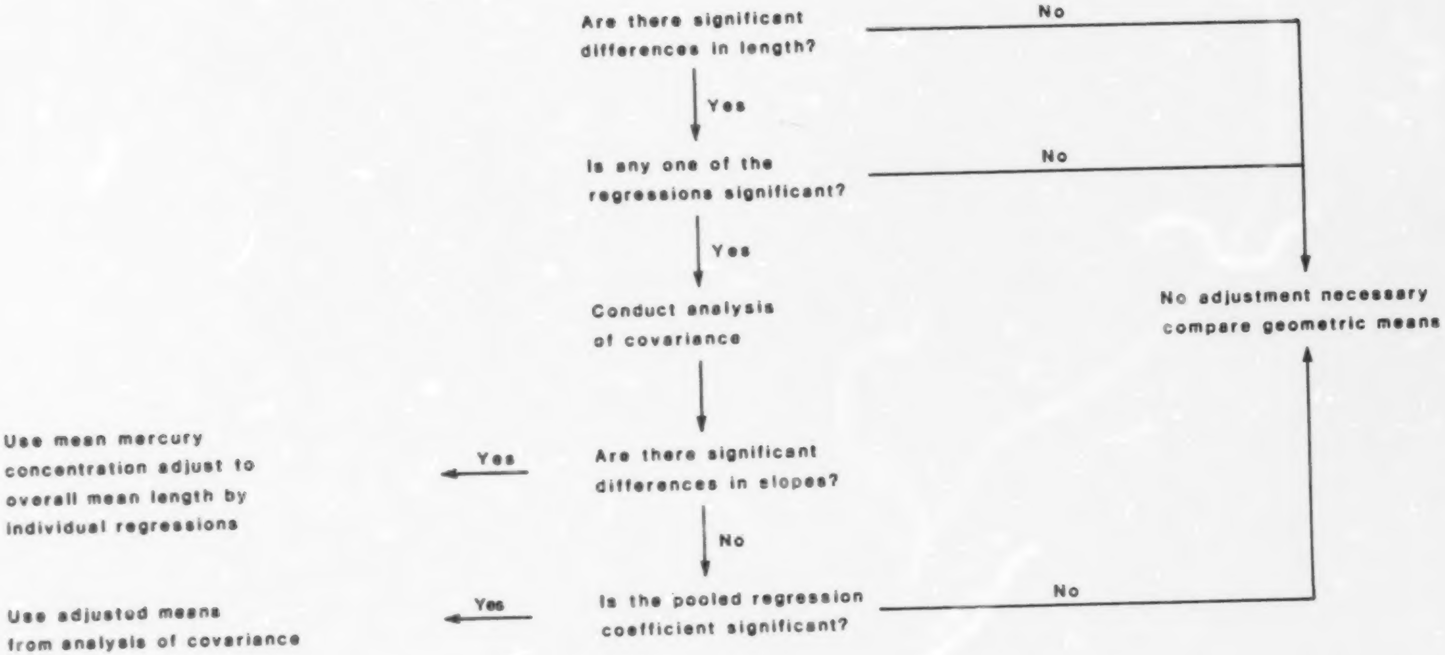
Are there significant differences in length?
No
Yes
Is any one of the regressions significant?
No
Yes
Conduct analysis of covariance
No adjustment necessary compare geometric means
Use mean mercury concentration adjust to overall mean length by individual regressions
Yes
Are there significant differences in slopes?
No
Use adjusted means from analysis of covariance
Yes
Is the pooled regression coefficient significant?
No

Figure 5.6 Procedure for adjusting mercury concentrations of sample for comparison purposes.

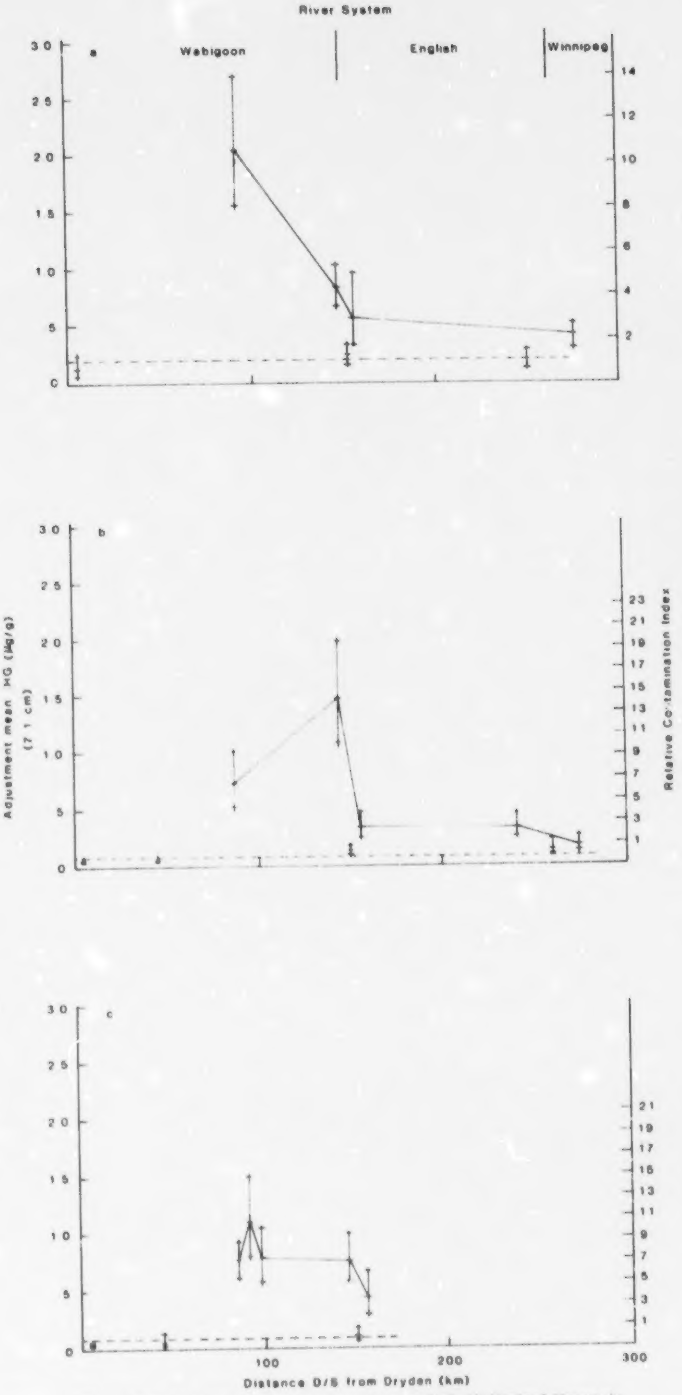

Figure 5.7 Mercury concentrations in crayfish abdominal tissue in the Wabigoon /English/Winnipeg River system: (a) 1979, (b) 1980 and (c) 1981. Dashed line represents mean of three or four control sites. (Relative contamination index explained in text, p. 6).

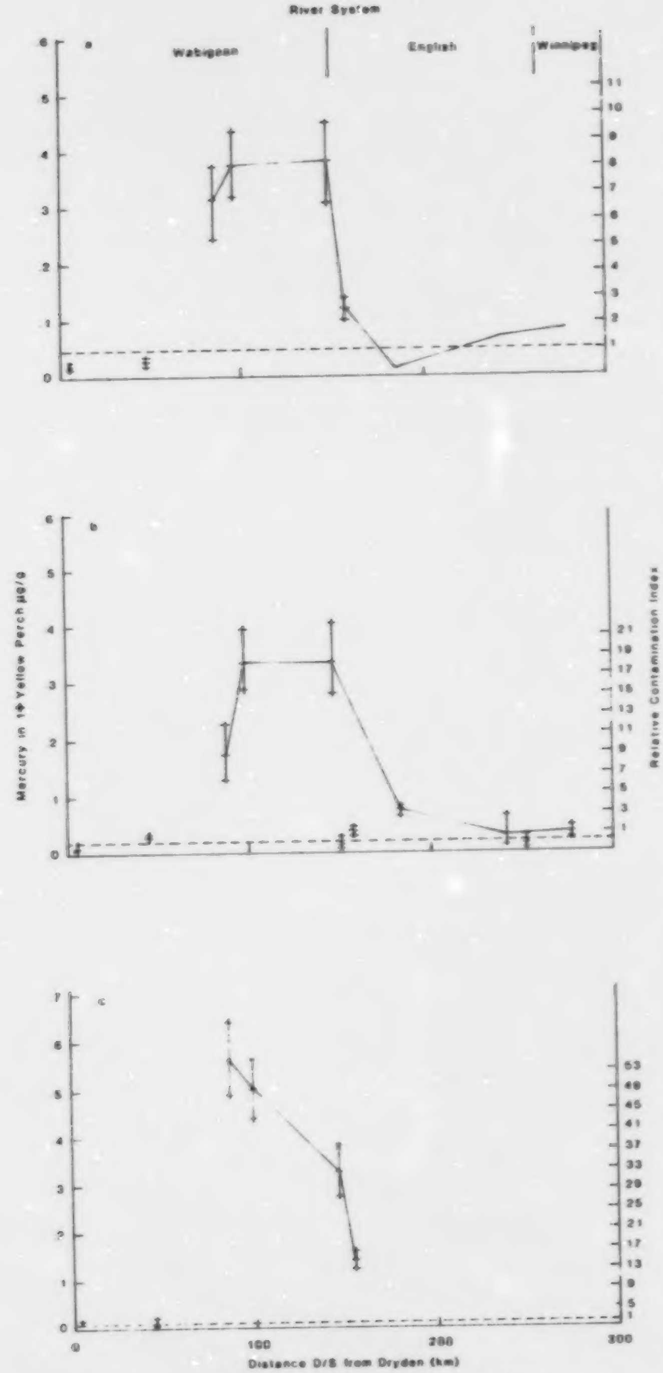

Figure 5.8 Mercury concentrations in 1+ yellow perch in the Wabigoon /English/Winnipeg River system: (a) 1979, (b) 1980 and (c) 1981. Dashed line represents mean of three or four control sites. (Data provided by Water Resources Branch Ontario Ministry of the Environment).

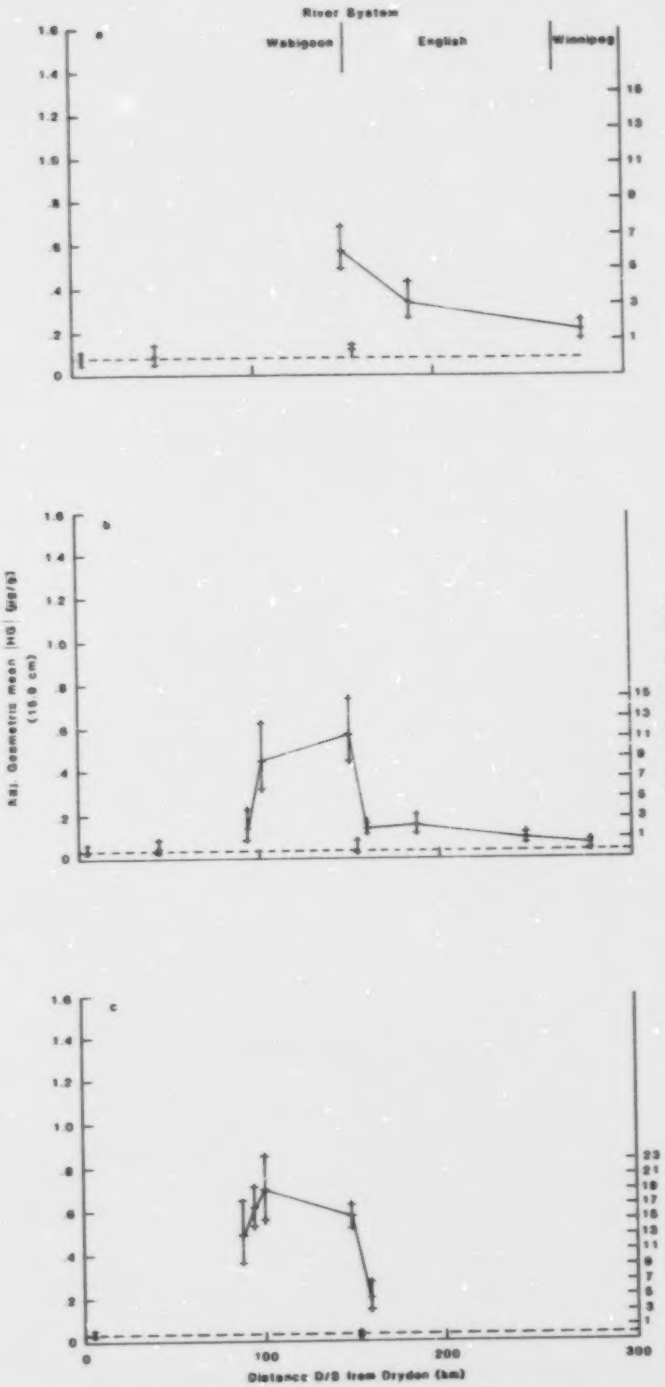

Figure 5.9 Mercury concentrations in 0+northern pike in the Wabigoon/English/Winnipeg River system: (a) 1979, (b) 1980 and 1981. Dashed line represents mean of two or three control sites.

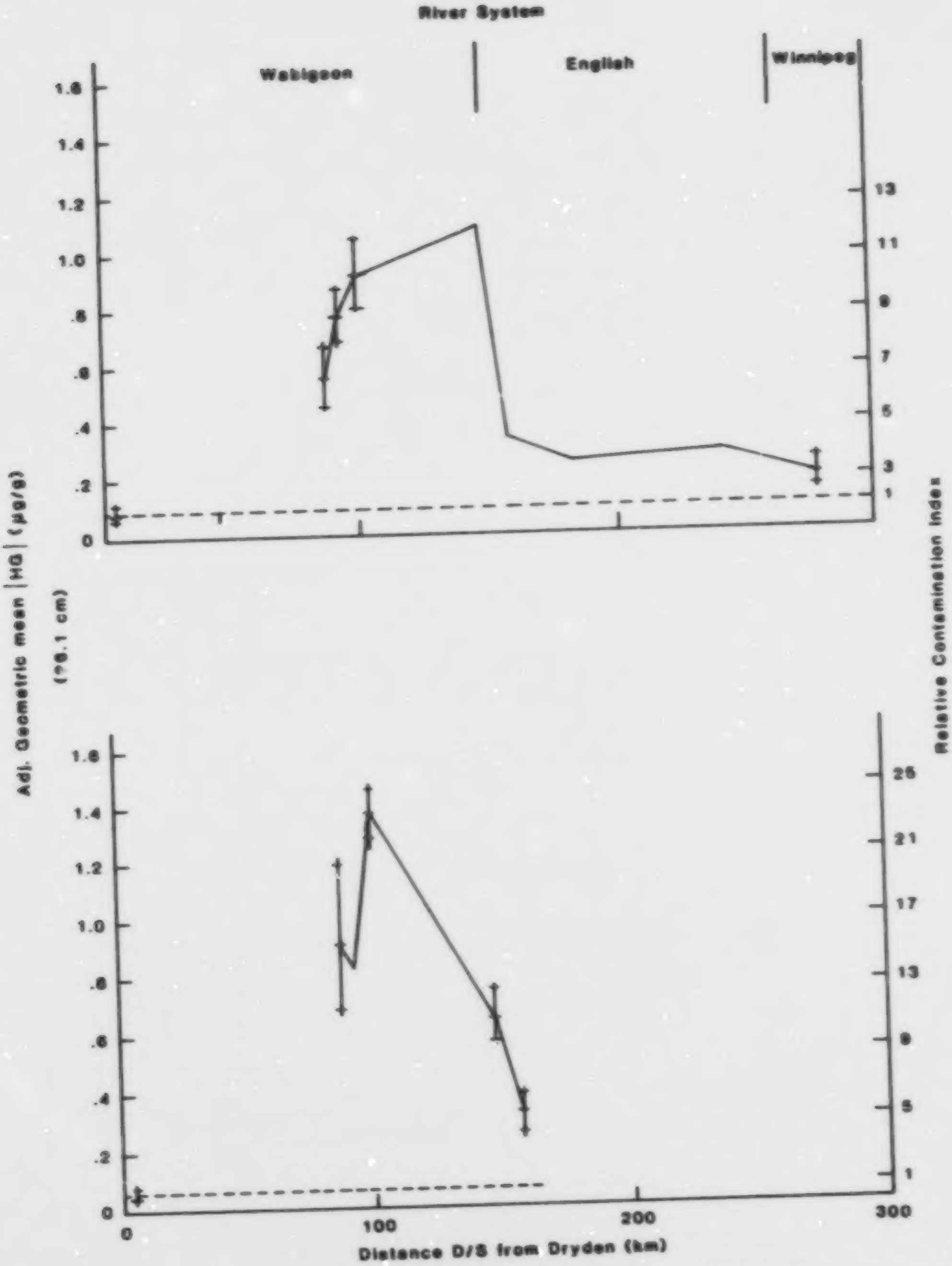

Figure 5.10 Mercury concentrations in 1+ northern pike in the Wabigoon/English/Winnipeg River system: (a) 1980 (b) 1981 Dashed line represents mean of three control sites.

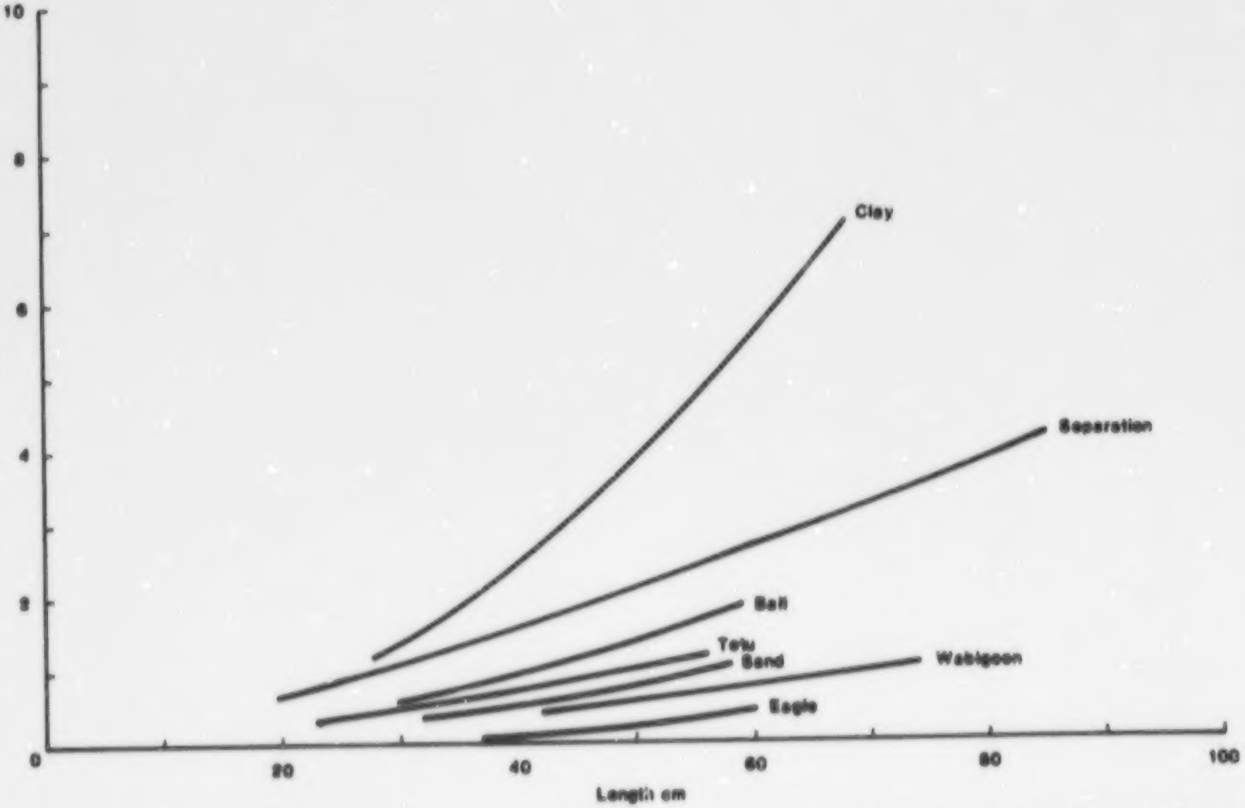

Figure 5.11 Mercury concentrations in adult walleye from seven lakes in the Wabigoon/English/Winnipeg River system, 1982. See Appendix 5C for Statistics.

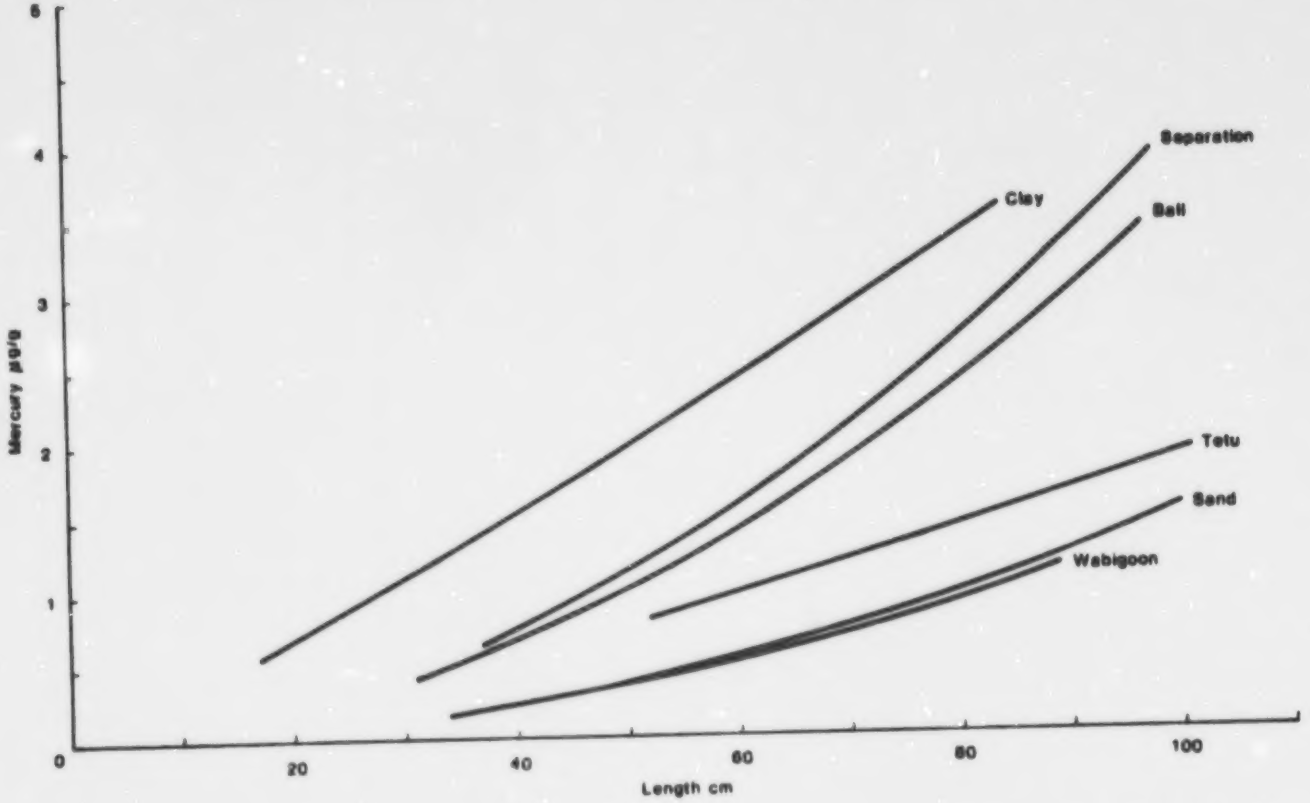

Figure 5.12 Mercury concentrations in adult northern pike from six lakes in the Wabigoon/English/Winnipeg River system, 1982. For statistics see Appendix 5C.

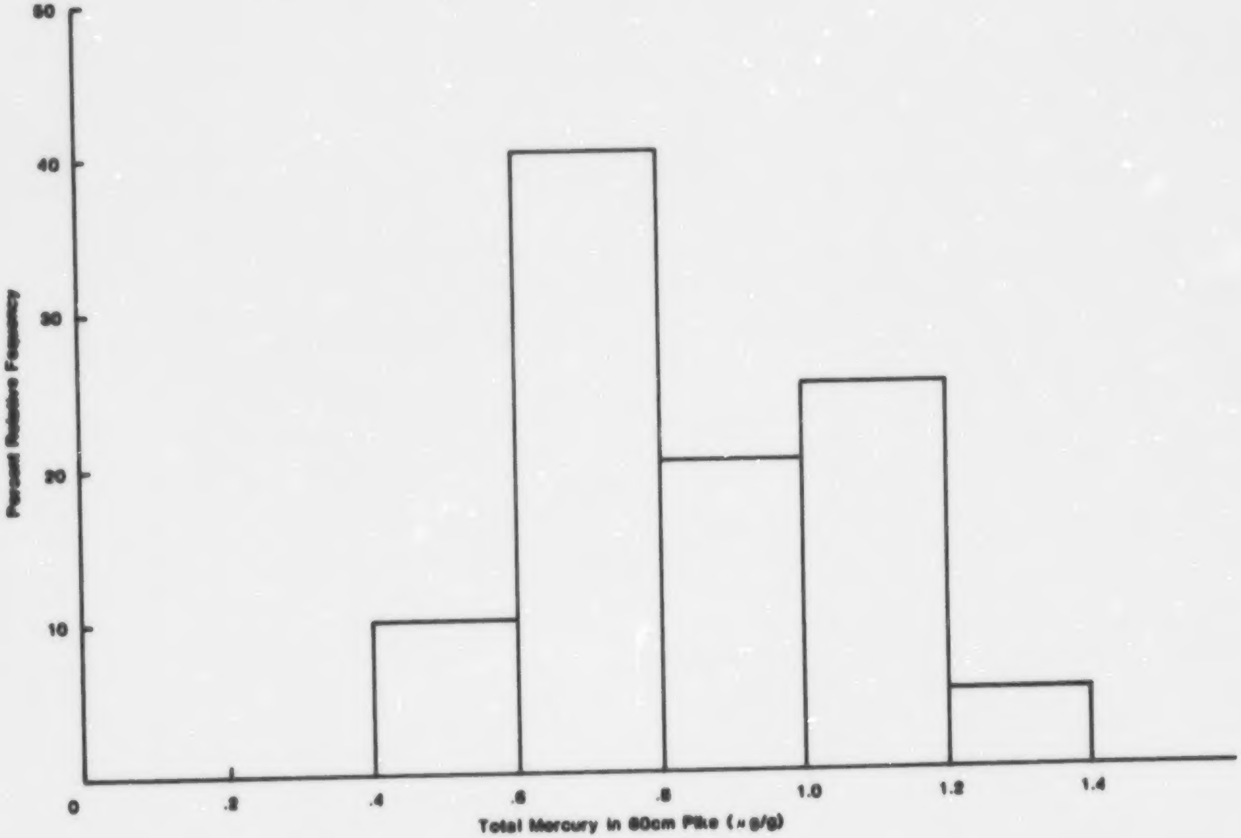

Figure 5.13 Mercury concentrations in 60-cm northern pike from 22 lakes in northwestern Ontario unaffected by discharge of waterborne mercury wastes. (Bishop and Neary, 1976).

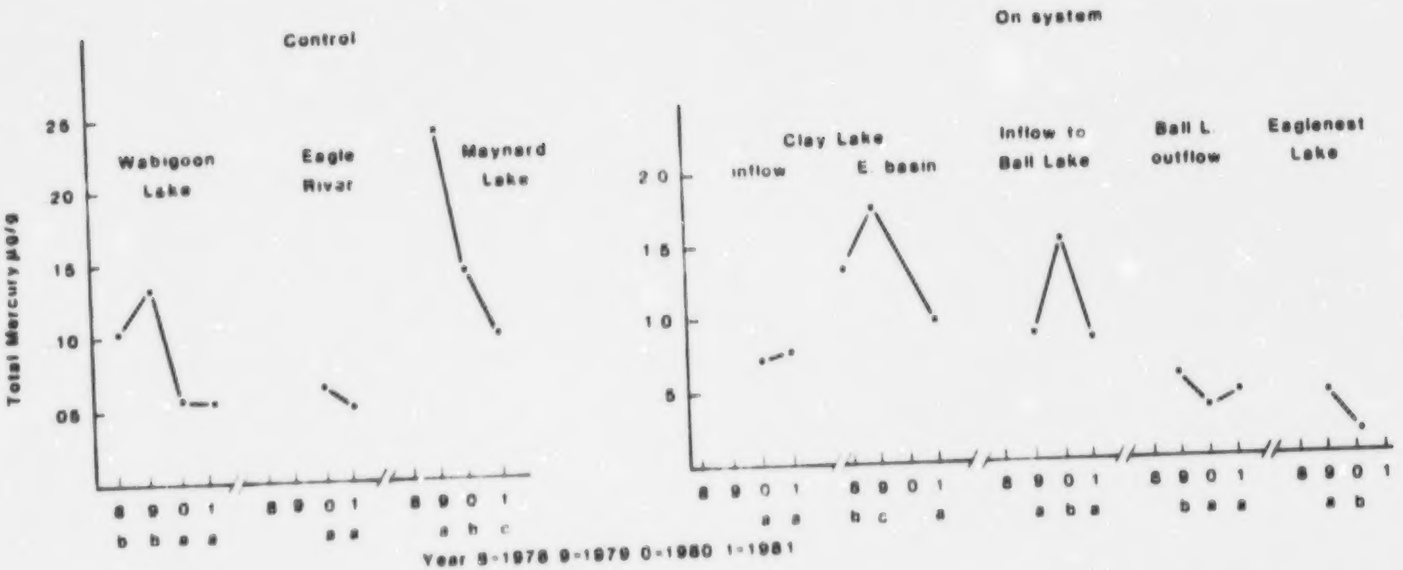

Figure 5.14 Temporal trends for mercury concentrations in crayfish abdominal muscle. See text (5.3 a) for statistical methods.

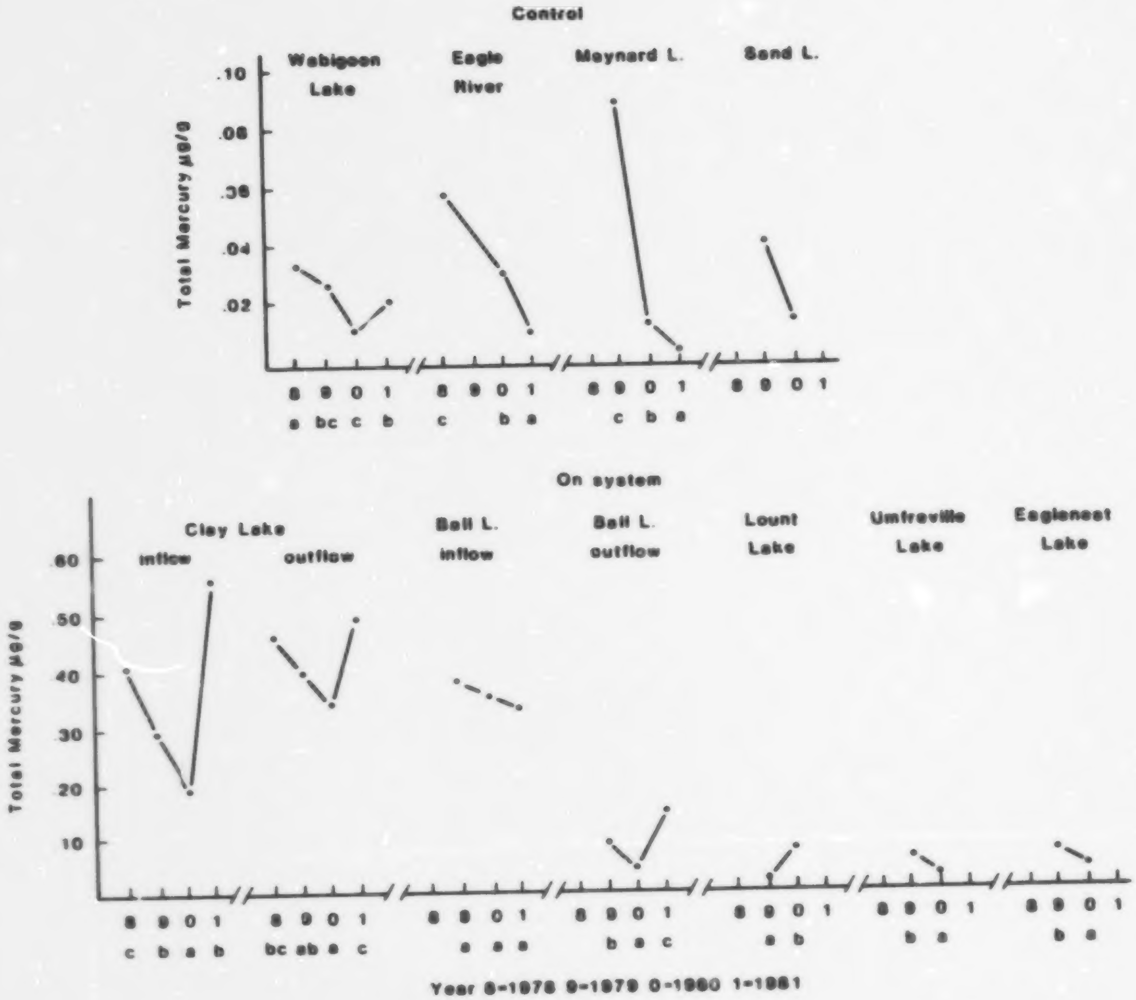

Figure 5.15 Temporal trends for mercury concentrations in 1+yellow perch. See text (5.3a) for statistical methods.

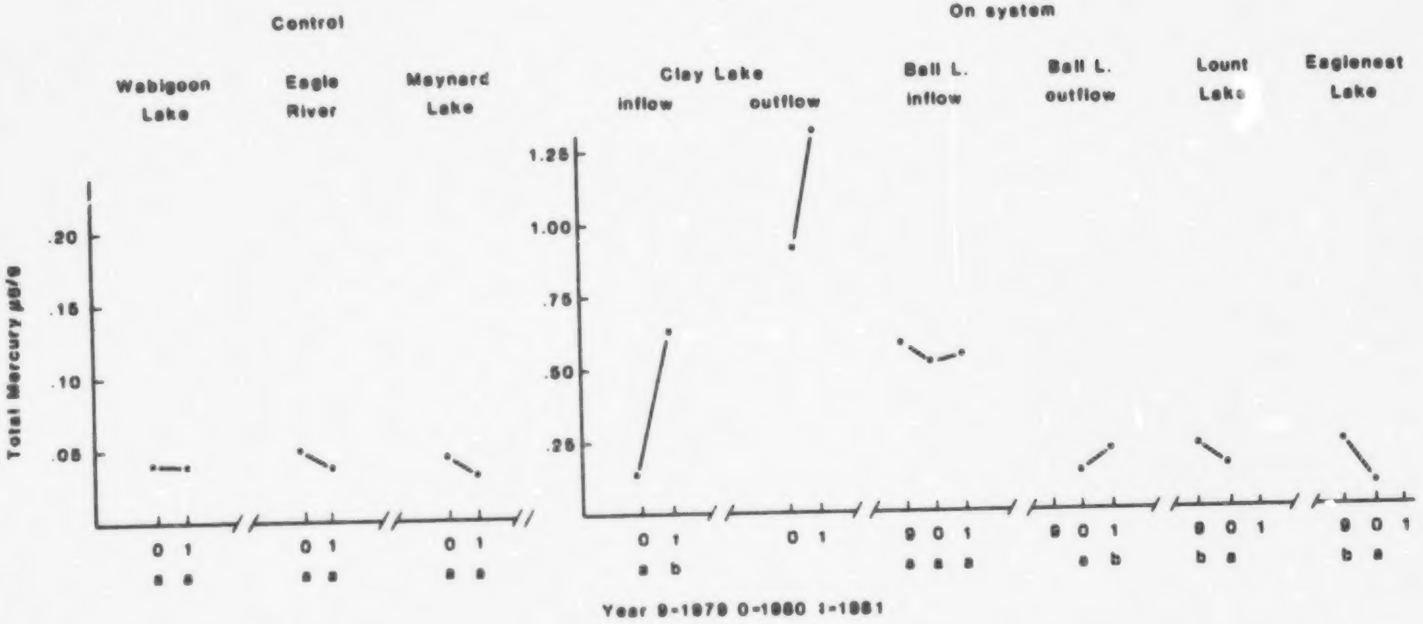

Figure 5.16 Temporal trends for mercury concentrations in 0+ northern pike. See text (5.3a) for statistical methods.

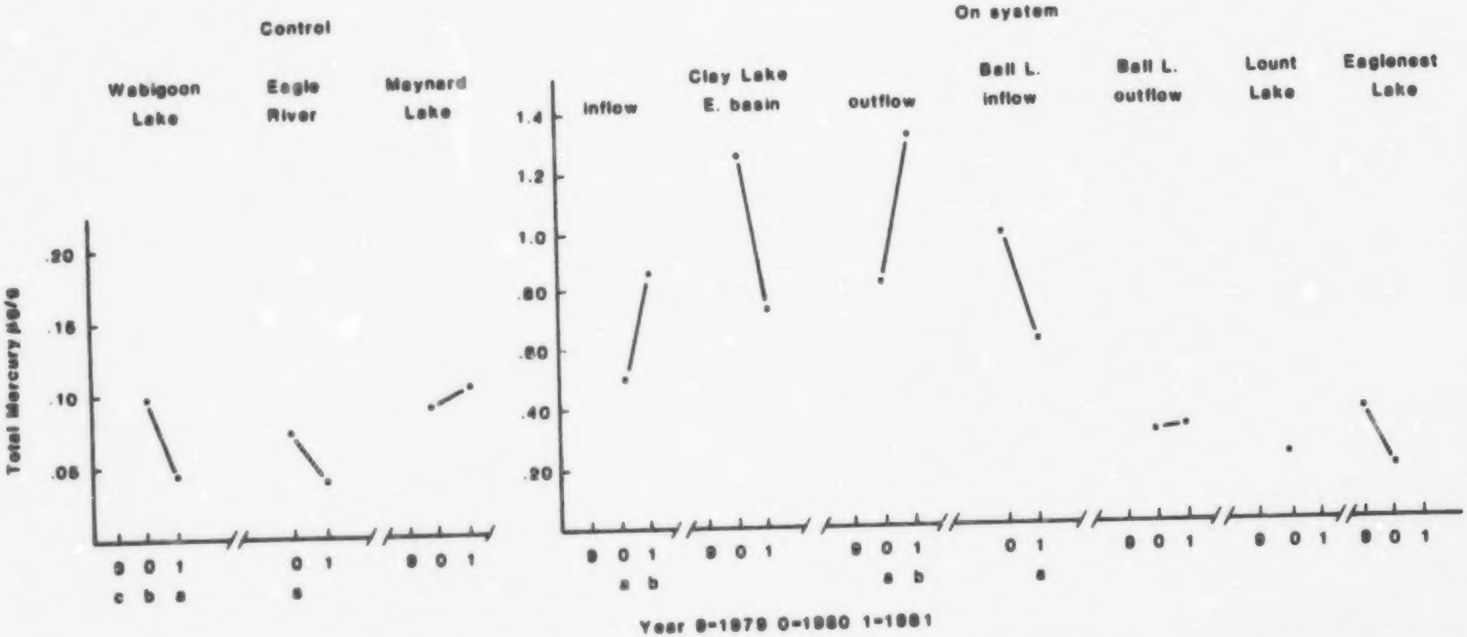

Figure 5.17 Temporal trends for mercury concentrations in 1+ northern pike. See text (5.3a) for statistical methods.

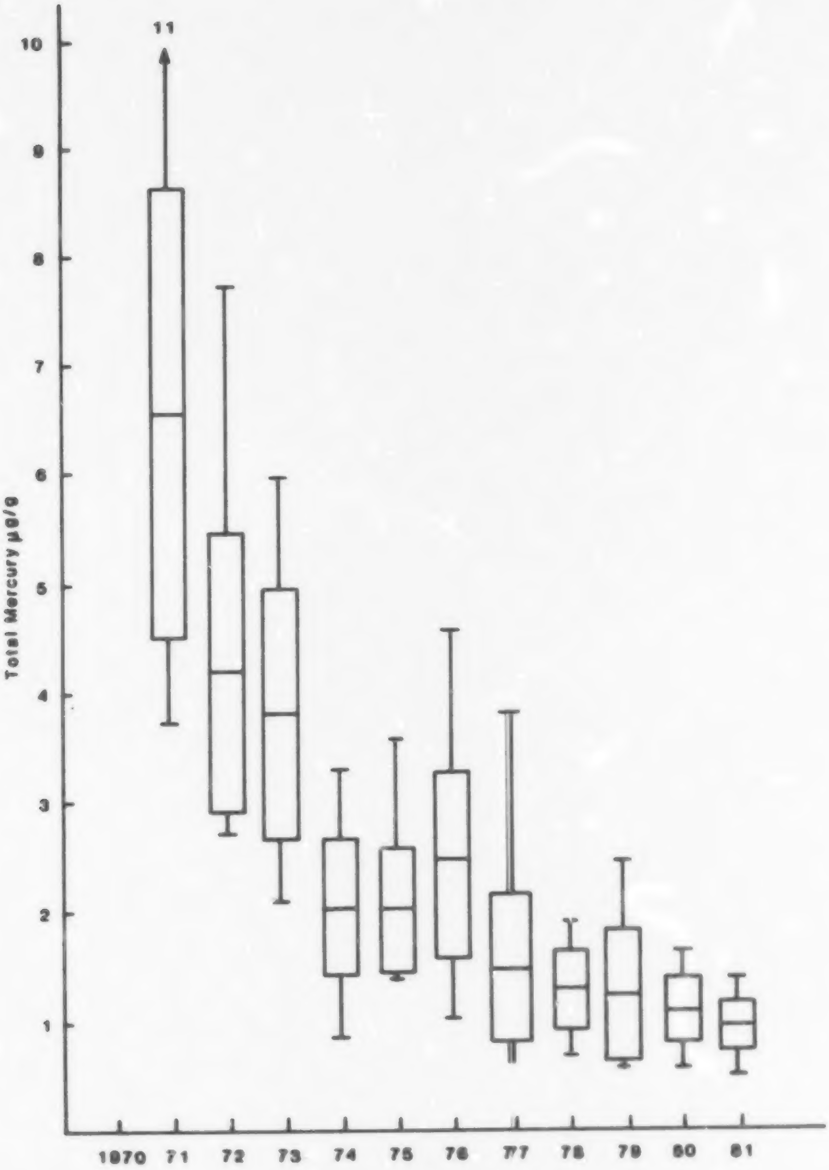

Figure 5.18 Mean, standard deviation and range of mercury concentrations in abdominal muscle of crayfish over 65cm in total length, Clay Lake, 1970-81. (A.L. Hamilton 1982).

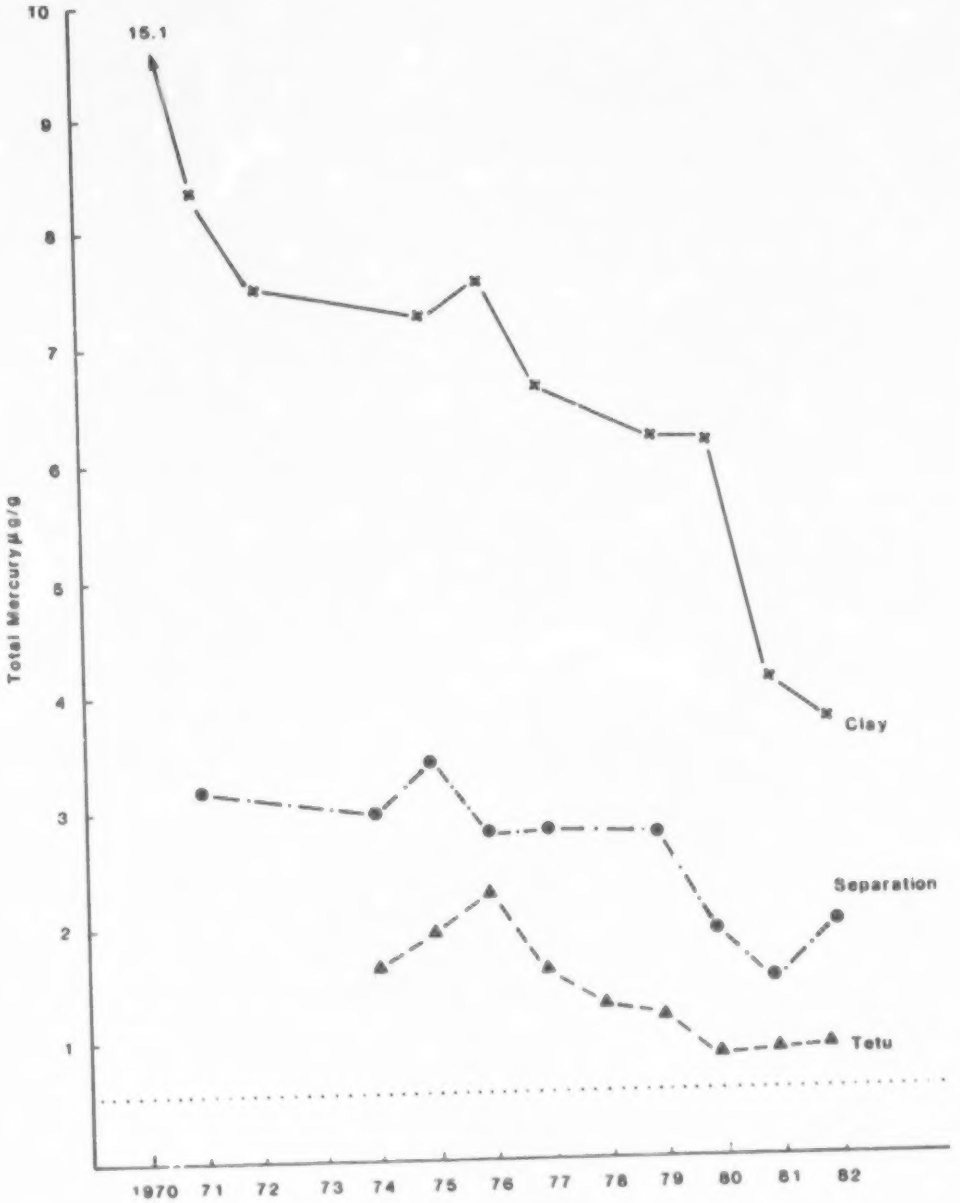

Figure 5.19 Mercury concentrations in 50cm walleye from three lakes on the Wabigoon/English/Winnipeg River system, 1970-82. Dotted line represents mean for on system four control lakes.

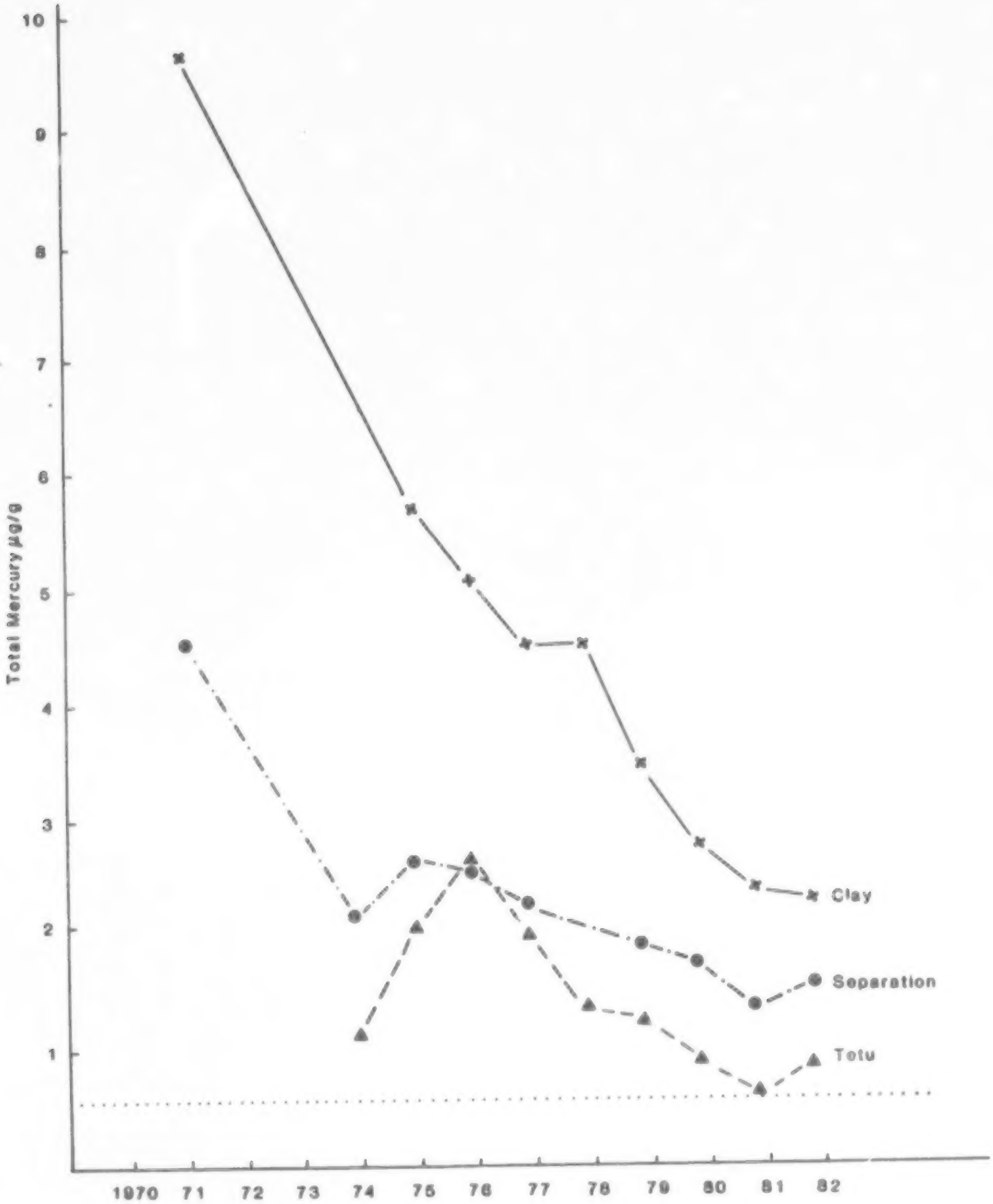

Figure 5.20 Mercury concentrations 60cm northern pike from three lakes in the Wabigoon/English/Winnipeg River system, 1970-82. Dotted line represents mean of four on system control sites.

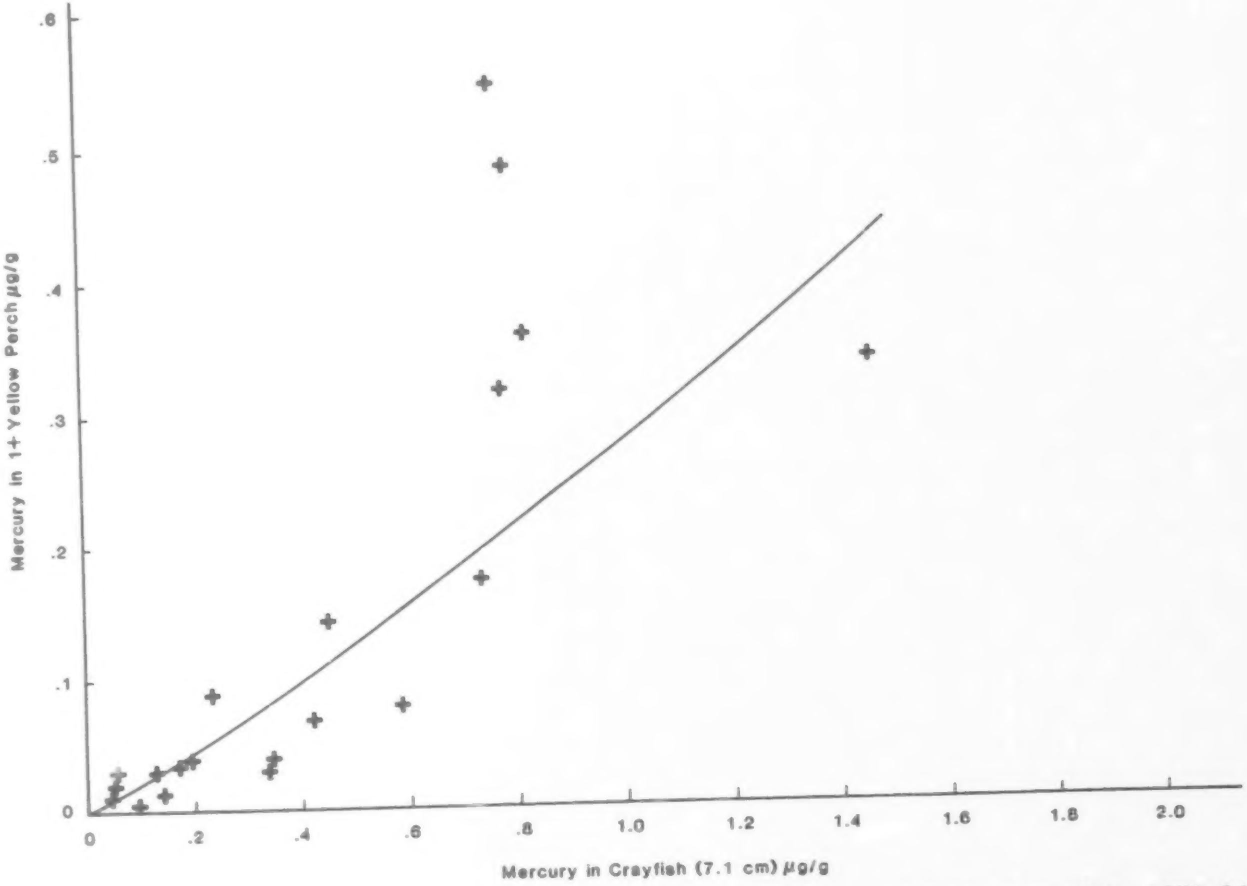

Figure 5.21 Relationship between total mercury levels in yellow perch and in crayfish , 1979-81. ($r=.88$ $p<.001$ $n=21$)

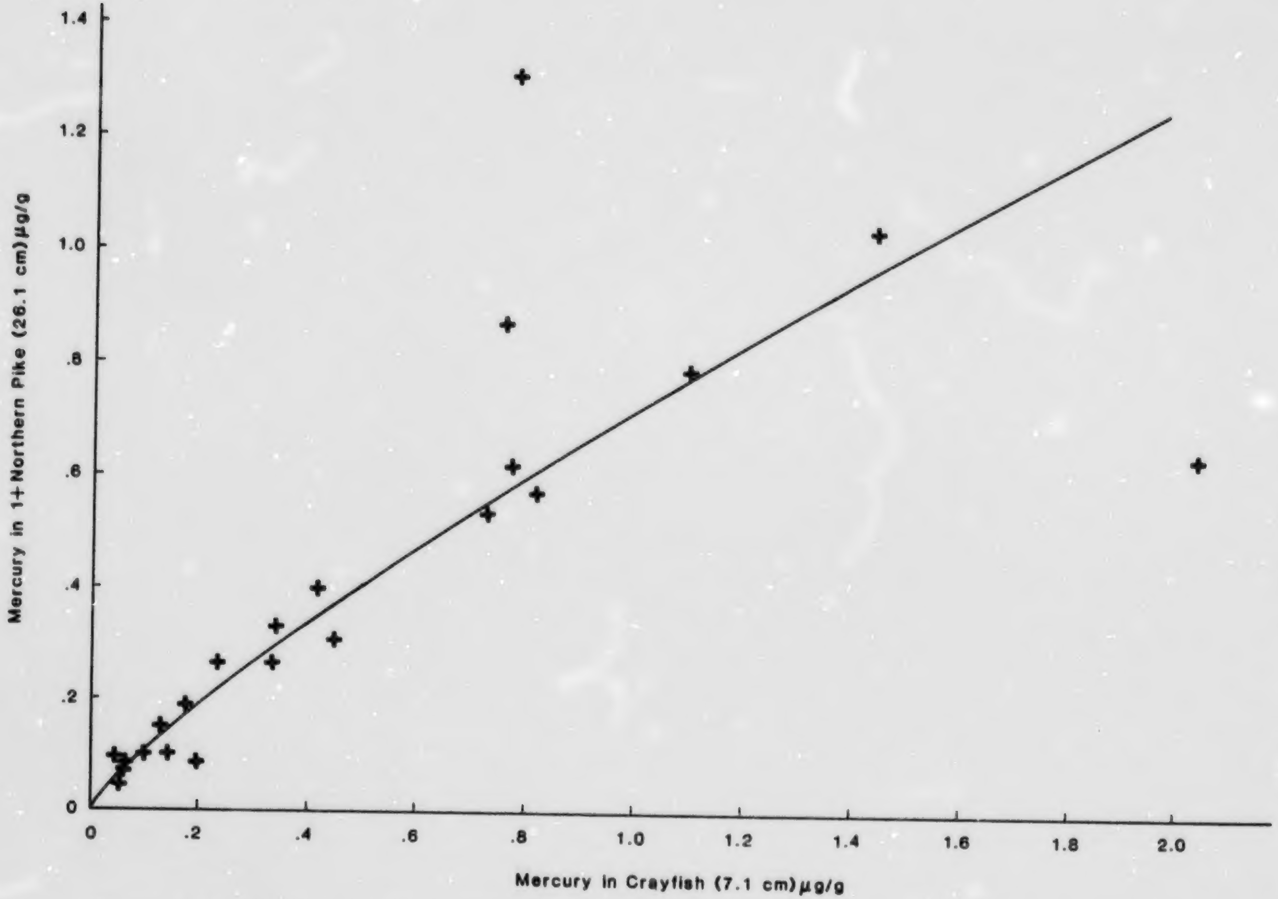

Figure 5.22 Relationship between total mercury levels in 1+northern pike and crayfish, 1979-81. ($r=.94$ $p<.001$ $n=22$)

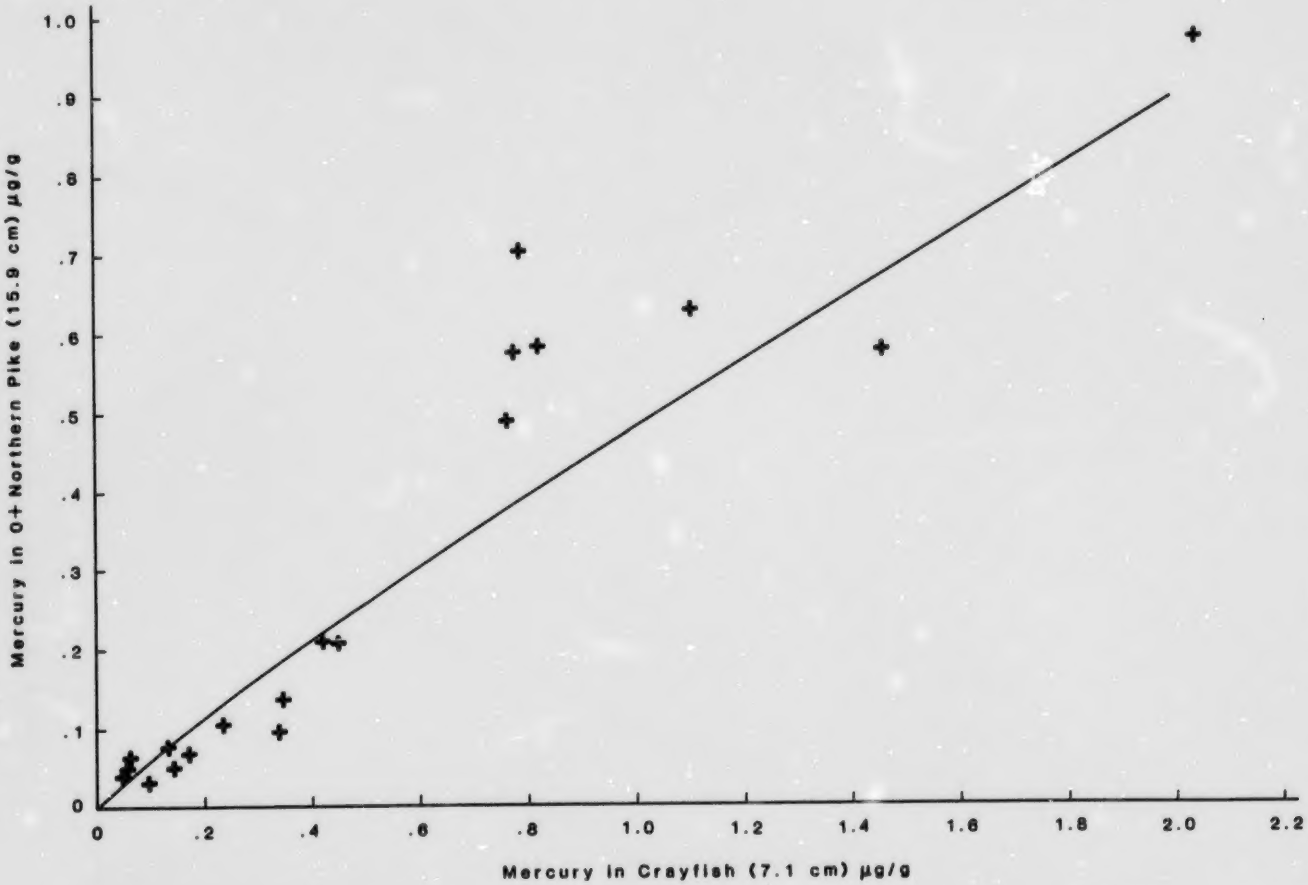

Figure 5.23 Relationship between mercury levels in 0+northern pike and crayfish , 1979-81.
(r=.95 p<.001 n=21)

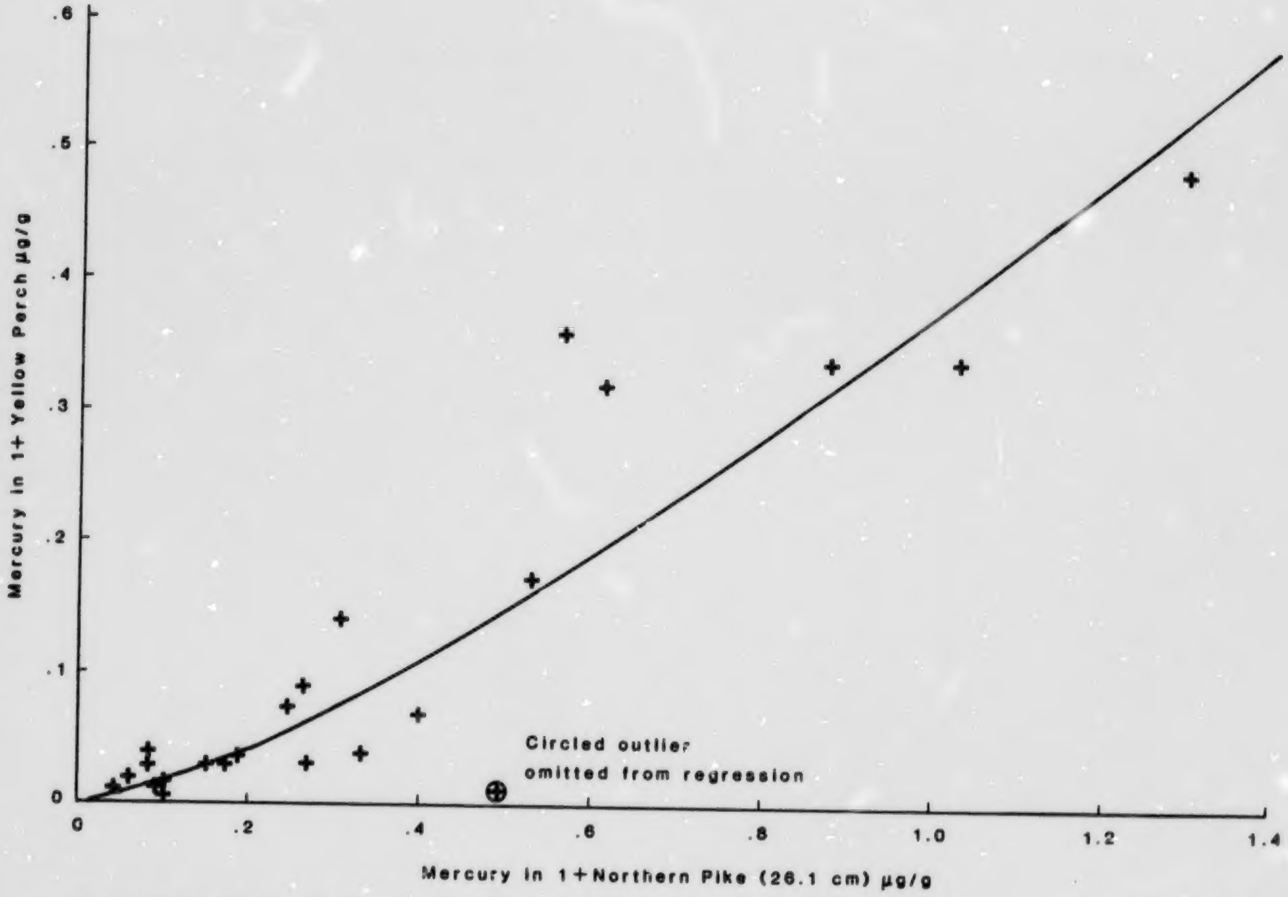

Figure 5.24 Relationship between mercury levels in 1+yellow perch and 1+ northern pike, 1979-81. (r=.82 p<.001 n=24)

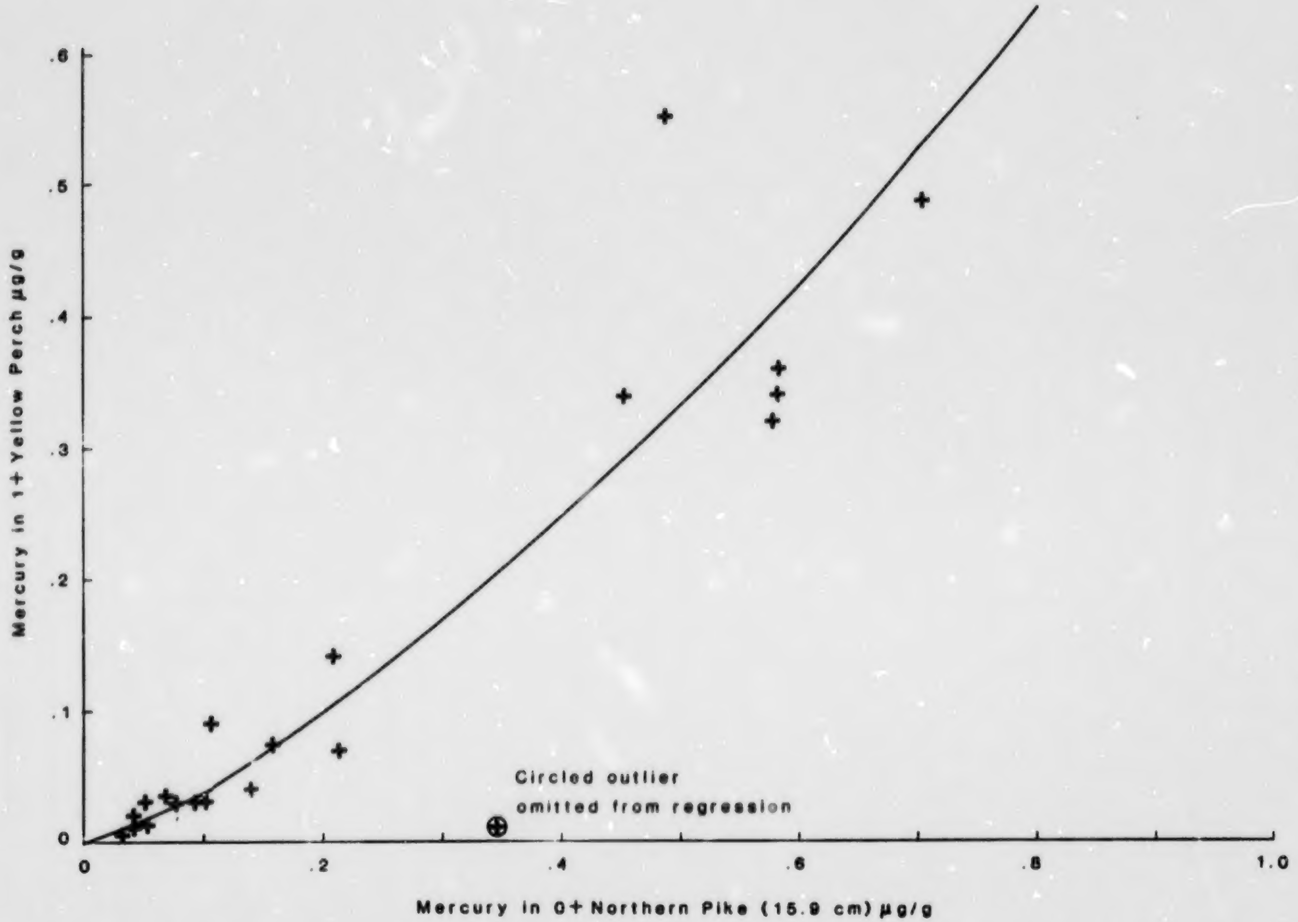

Figure 5.25 Relationship between mercury concentrations in 1+yellow perch and 0+northern pike, 1979-81.(r=.86 p<.001 n=22)

6. RELATIONSHIP BETWEEN MERCURY IN WATER, SEDIMENTS AND BIOTA

6.1 INTRODUCTION

In the preceding three sections of this report, we described total and methylmercury in water and total mercury in sediments and selected organisms. The purpose of this section is to describe relationships between mercury concentrations in sediment, water, and selected biota. The mechanisms involved in the transfer of mercury from one aquatic component to another were not assessed, but comments on key processes and variables affecting methylmercury levels in fish will be presented.

A "fixed" proportion of the mercury body burden in different biota is considered to be in the methyl form. The biogeochemical cycling of different forms of mercury between ecosystem components is complex (Miller, 1977; Norstrom, et al., 1976; Huckabee, et al., 1975). Many laboratory studies have attempted to describe relationships between mercury levels in aquatic environments (Gillespie, 1972; McKim, et al., 1976; Kudo and Mortimer, 1979). However, little work has been done with natural systems, largely due to their complexity and the analytical limitations for total and methylmercury in water.

6.2 METHODS

In natural aquatic systems, there are many problems in relating contaminant levels in biota to other properties of the system. Because mercury concentrations in freshwater animals are a function of their exposure, their movement and contaminant levels in the surrounding environment must be known. Although we cannot obtain exact exposure data for biota in natural systems, sampling procedures were standardized in this study to explain the relationships of mercury and methylmercury for specific sites. We selected freshwater species which: (1) were allopatric (came from different geographical parts of the ecosystem), (2) lived in a very localized area, (3) belonged to different trophic levels, and (4) usually had life spans for which exposure data were available or could be estimated.

Unfortunately, our data for biota (1979-81) do not correspond exactly to the data for water (1978-80). To obtain best use of our information, annual data were averaged for sites that had a similar chemical limnology. We believe that water and biota data which cover exactly the same period may not be necessary. Although concentrations of total and methylmercury in water are dynamic, and vary seasonally, their levels showed little change from year to year under normal hydrological conditions. Mercury concentrations in surface sediments in lakes of the ecosystem changed very slowly. Therefore, mercury levels in the surface layer (0-5 cm) of clay sediment were used in our calculations.

Data for total mercury in standardized samples of biota and in surface sediments for eight sites in the Wabigoon/English system appear in Table 6.1. The same table gives mean total and methylmercury concentrations in water under normal hydrological conditions. Clay and silt sediments, which are qualitatively similar, were used to provide data for developing relationships between compartments of the ecosystem.

6.3 RESULTS AND DISCUSSION

Relationships between mercury concentrations in biota, waters and sediments are summarized in Table 6.2. All regressions were statistically significant at the 95 percent probability level ($p<.05$). If exposure to methylmercury is elevated, an organism will have elevated methylmercury in its tissue. In this discussion, in vivo mercury methylation in pike, perch or crayfish is neglected. It has been shown by other researchers (Section 5) that the relative importance of food and water pathways of methylmercury into each organism is different. However, body burdens of methylmercury from food and water are additive (Norstrom, et al., 1976; Phillips and Buhler, 1978).

Section 5 revealed a strong, positive link between mercury in standardized pike and crayfish. To explain this relationship, we must know: (a) methylmercury levels in water, (b) the precise diet of each organism and (c) the source of methylmercury in each organism's diet. While adequate data were collected to answer item (a), data for (b) and (c) had to be obtained from the literature.

Upon hatching, young pike primarily consume aquatic insects. In several weeks, they begin eating young fish, and fish remain their main diet as adults (Scott and Crossman, 1973). Fish consumed by pike also derive their body burden of methylmercury from water and food. Even at this level in the food chain, methylmercury levels in water may account for much of the methylmercury in fish. For example, a study of perch (an omnivore and key component of pike diet) indicated that about 50 percent of its body burden could be ascribed to methylmercury levels in water (Norstrom, et al., 1976). Thus, methylmercury in water seems to play a major role in determining methylmercury body burdens in large predators. A predator-prey radiochemical experiment in Clay Lake showed that young pike could obtain 50-70 percent of their body burden from the water column (Turner and Swick, 1983).

Crayfish, on the other hand, appear to derive very little methylmercury from the water, and food is likely their prime source. Because of the varied feeding habits of crayfish, the source of their methylmercury is more difficult to determine than that for pike. On the other hand, their divergent sources of food make crayfish an excellent net "integrator", reflecting the level of mercury contamination in an ecosystem. The strong correlation between mercury in pike and crayfish, despite differences in habitat, diet, and methylmercury uptake routes, clearly indicates that methylmercury concentrations in water, sediment, and components of different food webs are all interrelated.

Empirical relationships between these ecosystem components are illustrated in Figure 6.1. Relationships in Figure 6.1 are numbered for use in the following discussion. Relationship #2 (between methylmercury in pike and in water) was expected and is confirmed in Figure 6.2 and Table 6.2 for all biota. Relationship #4 (between total mercury in pike and in water) is supported by data in Figure 6.3. The strength of this link was initially surprising, since 85 percent of the mercury in pike is in methyl form, whereas 95 percent of the mercury in water is in the inorganic form. Inorganic mercury in sediments must first be transformed into methylmercury (relationship #6), then accumulated by biota from water or food. Methylmercury levels in water depend on either mercury methylation in the sediments (relationship #7) and subsequent release (relationship #8) and/or methylation in the water column (relationship #10).

Investigations relating mercury levels in fish to mercury levels in sediments (Gillespie, 1972; Kudo and Mortimer, 1979; Akagi, et al., 1979; Jernelov, 1970; Langley, 1973; Gillespie and Scott, 1971), failed to show whether methylation mechanism #8 or #10 was the more important. In any event, in the Wabigoon system, sediments directly or indirectly govern methylmercury levels in waters. Relationships #11 and #12 were expected, based on data in Figure 6.4. In relationship #11, there is probably little direct effect of mercury levels in sediments on methylmercury levels in pike, since pike are not bottom feeders.

In Section 4, we concluded that methylmercury concentrations in a contaminated aquatic ecosystem reached steady-state within a few days. Methylmercury in each compartment may then be taken up by aquatic biota. The significance of each compartment to the methylmercury body burden for a particular organism would depend upon the organism's diet, habitat, metabolism and life span. Methylmercury levels in phytoplankton would be a function of methylmercury levels in water, whereas methylmercury levels in suckers would be related to methylmercury levels in water (respiration) and in sediments (food). Partitioning of total and methylmercury occurs very rapidly in comparison to the age of sport fish. Thus, amelioration proposals must address the partitioning of methylmercury between sediment and water rather than methylmercury production alone. Many studies assume that the key factor limiting methylmercury levels in fish is the continuous production of methylmercury in the environment. In the Wabigoon system, this is unlikely the case. At least one laboratory investigation supports the importance of partitioning (Akagi, et al., 1979). In the Wabigoon system, methylmercury levels are a unique property of each site. Under steady-state conditions, methylmercury in the water could arise from inorganic mercury methylated in the sediments, or from the water column, or both.

We believe we have a basic understanding of factors affecting methylmercury levels in fish in the system studied. Because of steady-state conditions and partitioning of inorganic mercury and methylmercury in and between various parts of the ecosystem, the pathways of methylmercury to fish need not be quantified before considering amelioration proposals. Thus, each site in the system is a separate subsystem, with mercury levels in sediments ultimately governing the levels of methylmercury in fish.

Conclusions drawn here may help explain results of studies on mercury in other ecosystems. In Sweden, Hultberg and Hasselrot (1981) found a strong relationship between methylmercury in plankton and total mercury in pike. Hildebrand, et al. (1980), in a river-reservoir system in Virginia and Tennessee, reported that mercury levels in two species of fish were strongly correllated with total mercury concentrations in water, total dissolved mercury levels in water, total mercury in standardized sediment, and total mercury in benthic invertebrates. The relatively rapid partitioning of mercury could explain their observations.

The relationships discussed to this point apply to normal hydrological conditions, in which industrial wastes introduced at Dryden are largely assimilated upstream of Clay Lake. Changes to the biogeochemistry of the system, however, can strongly affect these relationships. Under normal conditions, we expect mercury in biota to slowly decrease over time (Hamilton, 1982; Parks, et al., Section 5). However, biota collected in 1980 at the eastern basin and inflow of Clay Lake had much lower mercury concentrations than those sampled the previous year, depsite higher methylmercury levels in water at both sites in 1980 than in 1979 or 1978. Further evidence for differences in bioavailability of methylmercury are presented in Figure 6.5 where mercury concentrations are plotted for 0+ and 1+ pike captured at the same site. The circled point is an outlier and represents fish collected at the eastern basin of Clay Lake in 1980. This point indicates that, in comparison to the general trend, levels of mercury in 0+ pike were much lower than expected, and it suggests a marked decrease in the bioavailability in methyl mercury for this site and time.

Decreased bioavailability of methylmercury in the eastern basin of Clay Lake may be related to changes in lake water chemistry, caused by the inability of the Wabigoon River to assimilate industrial discharges at Dryden during very low flows. According to basic thermodynamic principles, methylmercury in freshwater devoid of reduced sulphur compounds should be bound to hydroxides or chlorides (Baughman et al., 1973; Rabenstein, et al., 1975; Reimers and Krenkel, 1974). During typical hydrological conditions in the Wabigoon River, most organic wood wastes discharged into the river at Dryden settle out or are oxidized upstream of Clay Lake. Under very low flows (e.g.: 1980), all wastes are not oxidized in the river, and volatile reduced sulphur compounds are present (as evidenced by odour) downstream to the eastern basin of Clay Lake. Because of the well known affinity of methylmercury for anionic sulphur ligands (Table 17.3 in Carty and Malone, 1979), much of the methylmercury in the eastern basin of Clay Lake was probably tightly bound by sulphur compounds and less bioavailable than the weakly bound chloride and hydroxide complexes.

Ligand exchange reactions for methylmercury are very rapid (Rabenstein, 1978; Baughman, et al., 1973), even for sulfhydryl complexes which are very stable (Rabenstein, 1978). Thus, it is likely that partitioning of various methylmercury complexes in water is probably achieved within hours or so. From comparing methylmercury relationships with other parameters at the inflow and outflow of the Wainwright Dam, one may conclude that methylmercury is quite labile. Here, the average theoretical residence time under mean annual flows is estimated at 5 hours, a sufficient period to permit substantial changes in methylmercury binding. Thus, the bioavailability of methylmercury in this system is probably governed by environmental changes, not ligand exchange reactions.

CONCLUSIONS

1. Statistically significant empirical relationships for mercury and methylmercury are evident in and between water, sediment and biota in the Wabigoon/English/Winnipeg River system. Because of these links, the fraction of the mercury body burden in biota derived from food or water need not be established. Each site in the system studied can be viewed as a separate subsystem, with mercury concentrations in surface sediment ultimately governing methylmercury concentrations in fish. The level of contamination at each site can change, however, under the influence of mercury loadings from upstream sources, export of mercury to sites farther downstream, losses to the atmosphere, and burial of contaminated sediment.
2. Changes in water chemistry induced by anthropogenic loadings at Dryden can strongly affect the bioavailability of methylmercury.
3. The binding of methylmercury in water is probably governed by environmental changes in the water column, not exchange reactions of methylmercury itself.

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TABLE 6.1. Summary of mercury data used to generate relationships between biota, water, and sediment.

Site	Biota[a]				Water[b]	Water[c]	Sediment[d] (0-5 cm)
	0+ Pike (15.9 cm)	1+ Pike (26.1 cm)	Perch	Crayfish (7.1 cm)			
Wabigoon Lake	0.04	0.08	0.02	0.08	7	0.32	0.01
Eagle River	0.04	0.06	0.02	0.06	3	0.18	0.04
Clay Lake inflow	0.49	0.87	0.42	0.77	26	1.4	2.4
Clay Lake, eastern basin	0.63	0.75	-	1.6	24	1.3	3.0
Clay Lake outflow	0.59	1.10	0.40	0.79	16	1.3	2.8
Wabigoon River, inflow to Ball Lake	0.58	0.81	0.34	1.0	14	1.0	0.92
English River, inflow to Ball Lake	0.06	0.10	0.04	0.16	5	0.25	0.07
English River, outflow of Ball Lake	0.18	0.30	0.09	0.46	8	0.22	0.24

[a] Total Hg, µg/g.

[b] Total Hg, ng/ℓ.

[c] Methyl Hg, ng/ℓ.

[d] Total Hg, µg/g, dry weight.

TABLE 6.2. Correlation coefficients and significance levels for relationships between log transformed mercury concentrations in biota, water and sediments of the Wabigoon/English River system, 1979-81.

	1+ Pike	1+ Perch	Crayfish	Total Hg[a] in Water	MeHg[b] in Water	Sediment[c] (0-5 cm)
0+ Pike (15.9 cm)	$r = .99$	$r = .99$	$r = .98$	$r = .63$ $p<.05$	$r = .70$ $p<.05$	$r = .97$ $p<.01$
1+ Pike (26.1 cm)		$r = .99$	$r = .96$	$r = .67$ $p<.05$	$r = .72$ $p<.05$	$r = .96$ $p<.01$
1+ Perch			$r = .97$	$r = .91$ $p<.01$	$r = .90$ $p<.01$	$r = .86$ $p<.01$
Crayfish (7.1 cm)				$r = .90$ $p<.01$	$r = .84$ $p<.01$	$r = .94$ $p<.01$
Total mercury in water					$r = .94$ $p<.01$	$r = .86$ $p<.01$
Methylmercury in water						$r = .87$ $p<.01$

[a] ng/ℓ.

[b] ng/ℓ.

[c] μg/g, dry weight.

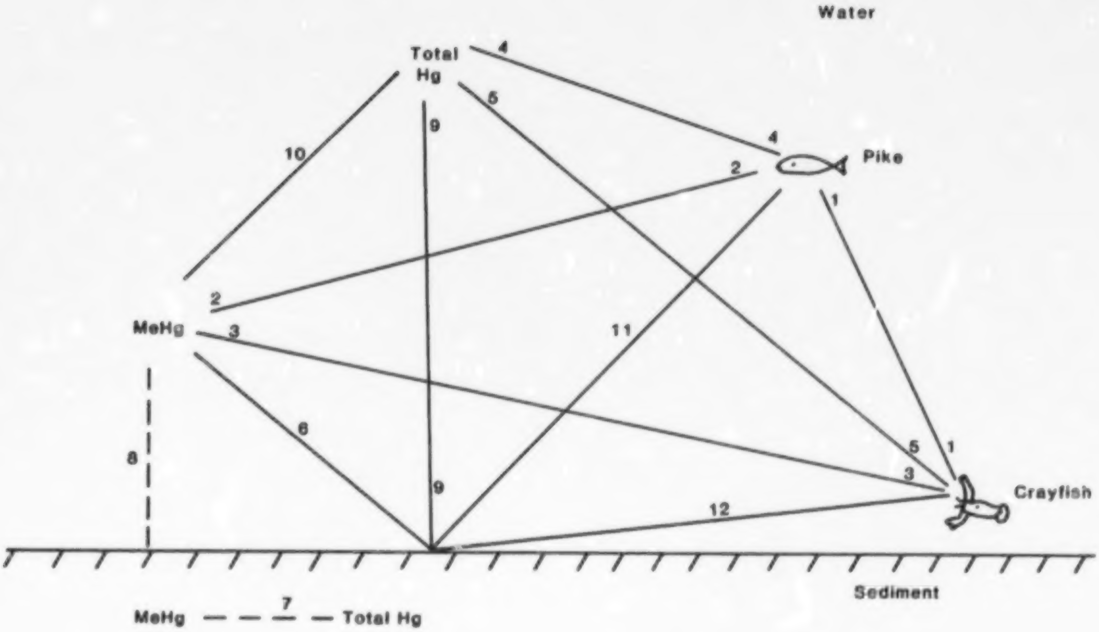
Water
Total Hg
4
5
10
9
4
2
Pike
1
2
MeHg
3
11
6
8
5
1
3
9
12
Crayfish
Sediment
MeHg
7
Total Hg

Figure 6.1 Empirical relationships between mercury in water, sediment and biota in the Wabigoon/English/Winnipeg system. (See table 6.2)

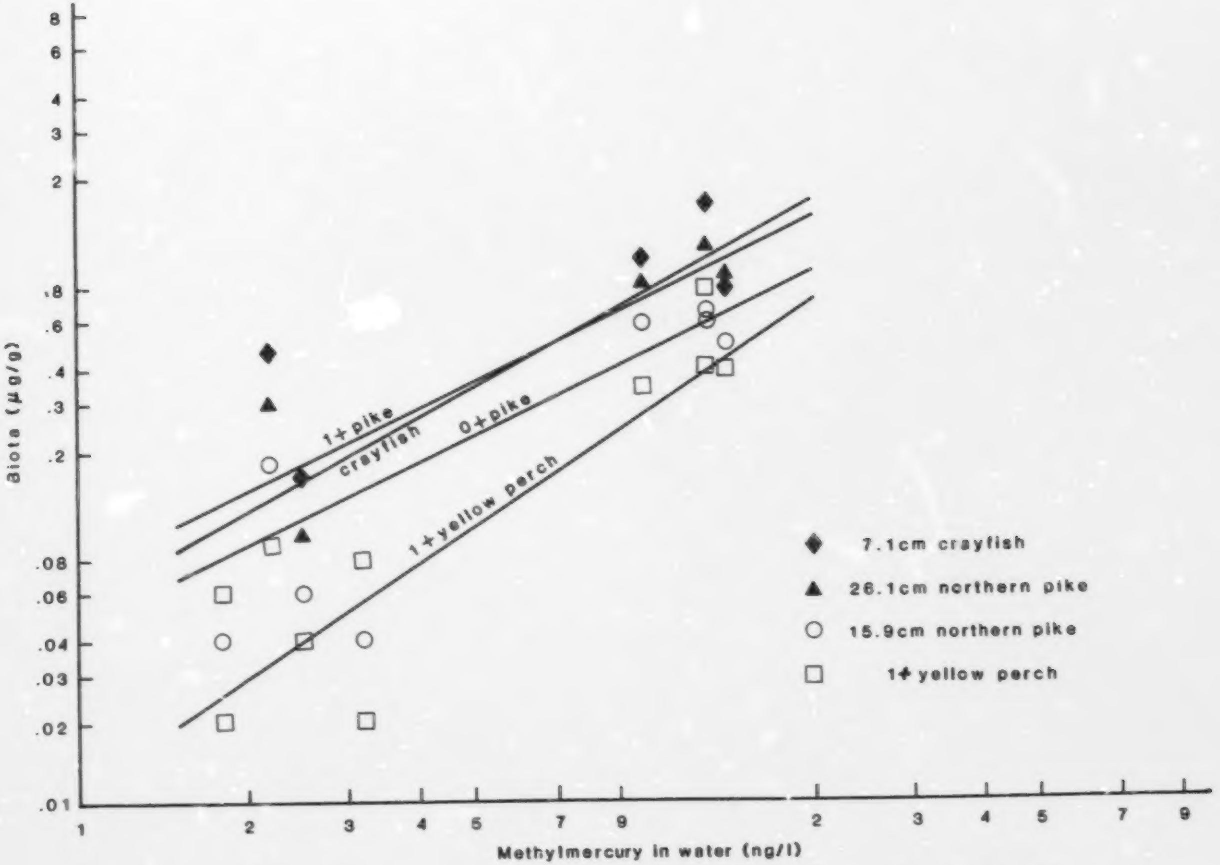

Figure 6.2 Relationships between total mercury concentrations in selected biota and methylmercury concentrations in water, Wabigoon/English River system, 1978-81.

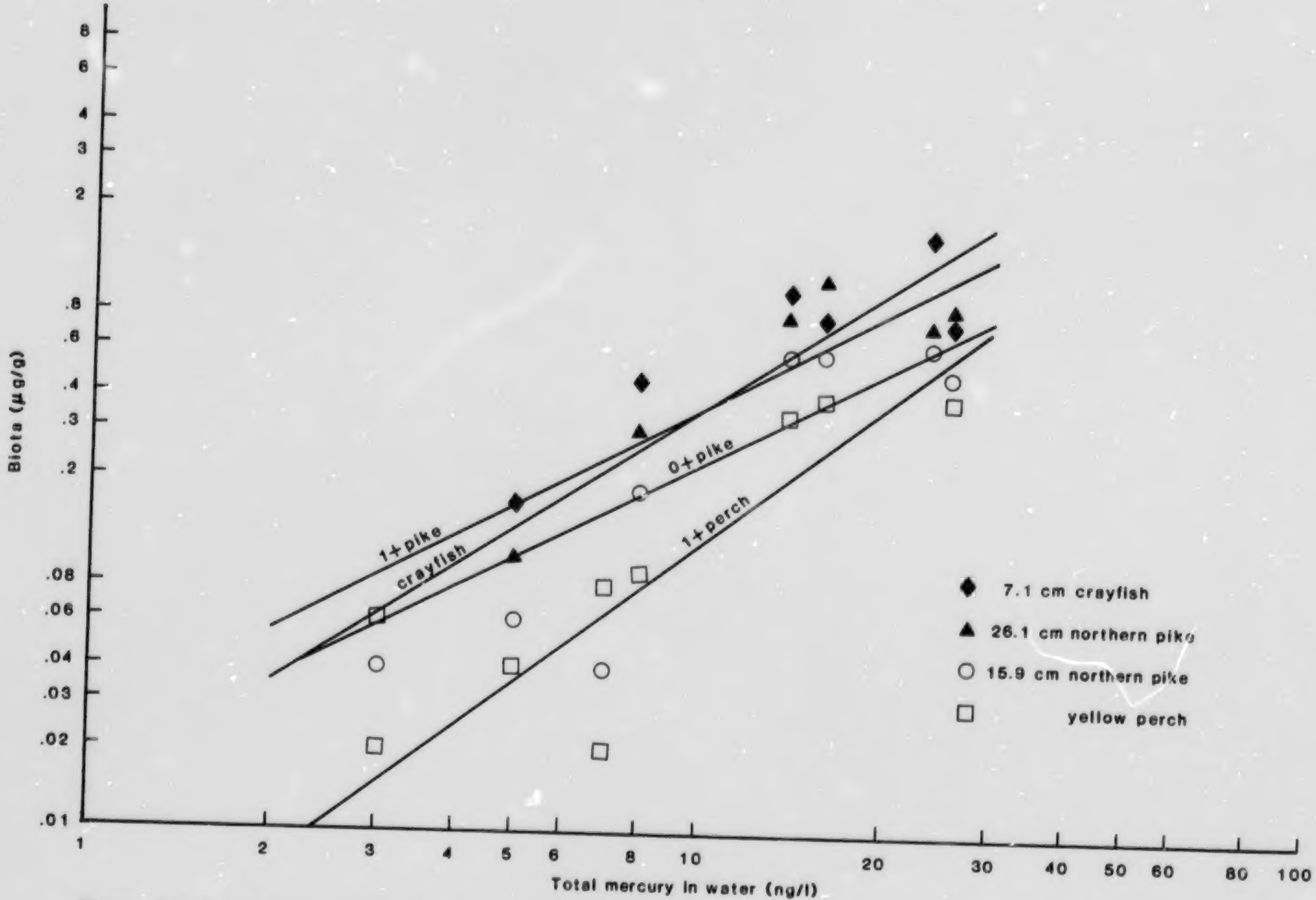

Figure 6.3 Relationships between total mercury concentrations in selected biota and total mercury concentrations in water, Wabigoon/English River system 1978-81.

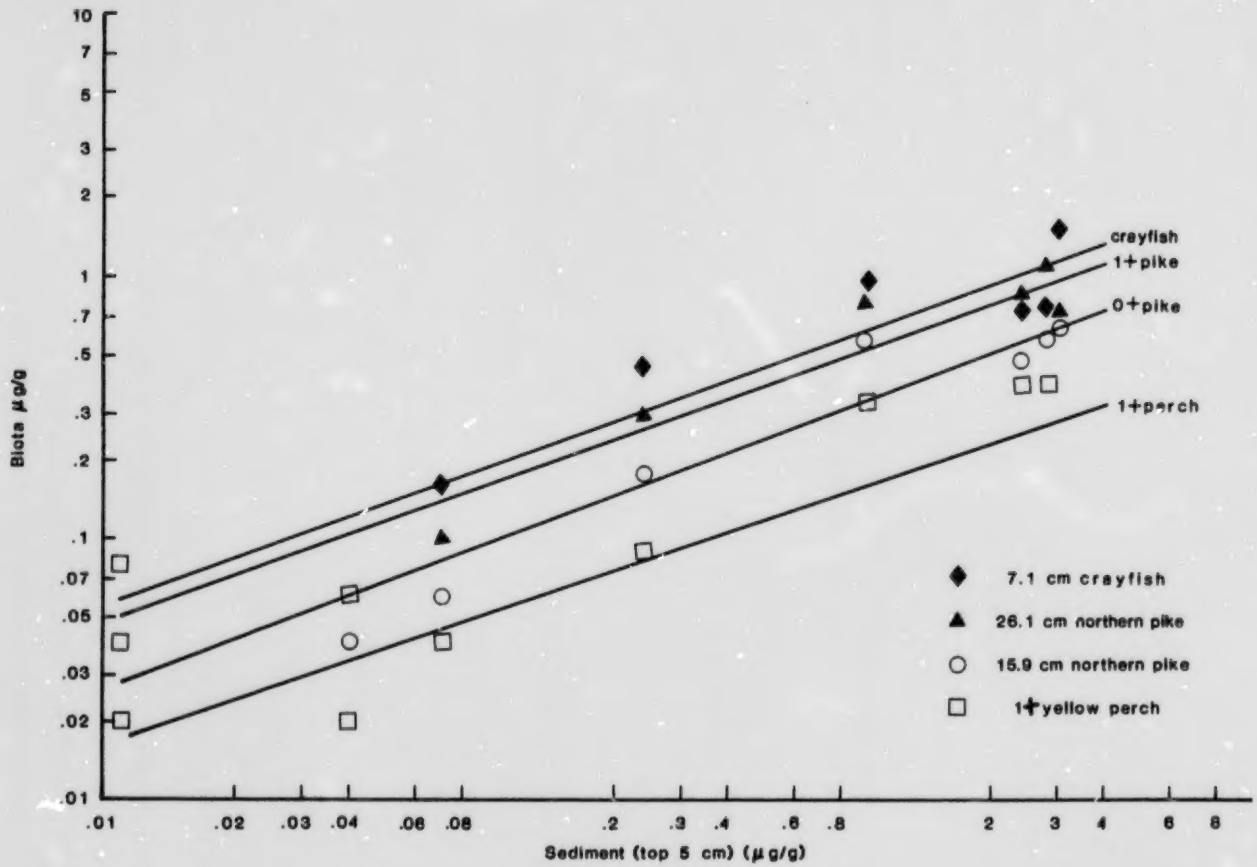

Figure 6.4 Relationship between total mercury concentrations in selected biota and in surface sediment, Wabigoon/English River system 1979-81.

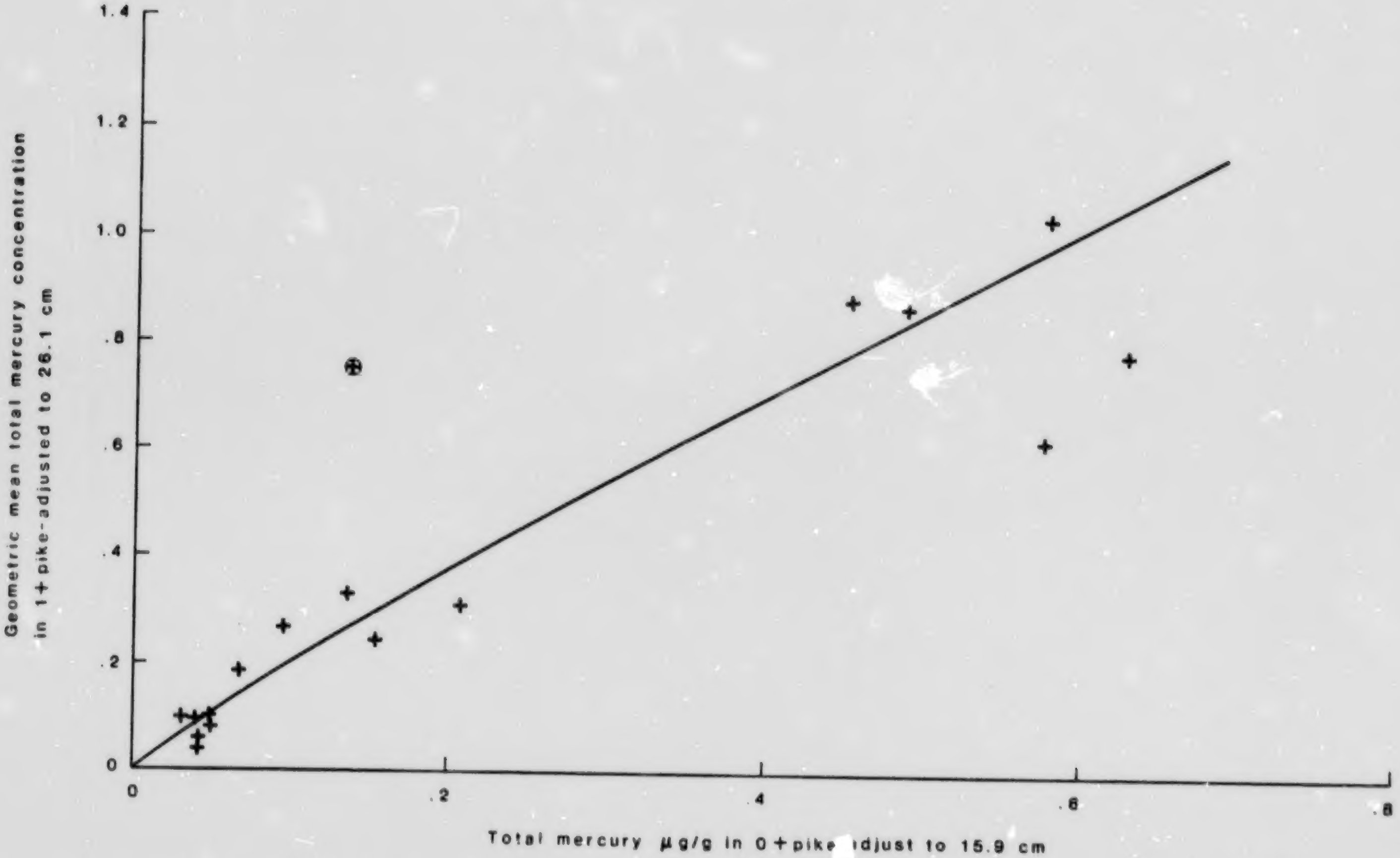

Figure 6.5 Relationship between total mercury levels in two age classes of northern pike, Wabigoon/English River system, 1979-81.

7. EFFECTS OF DISCHARGES FROM GREAT LAKES FOREST PRODUCTS ON MERCURY IN THE RECEIVING STREAM

7.1 INTRODUCTION

In Dryden, unregulated mercury losses from a chlor-alkali plant (associated with a pulp and paper mill) were estimated to be 1,100 kg per year between 1962 and 1969 (Table 7.1). When biota in the Wabigoon River system were found to contain excessive levels of mercury, abatement measures were taken in 1970. By 1971, losses from the chlor-alkali plant were under 10 kg annually, or less than 1 percent of former releases. Although the mercury cells were dismantled in 1975, residual annual mercury losses of about 2 kg continued. In the progress report of this study (Parks, et al., 1980), it was calculated that 15 kg was discharged from the total pulp and paper mill complex at Dryden for a 1-year period beginning in August, 1978. Apparently, 13 kg of mercury in the total effluent came from sources other than the chlor-alkali plant, although these were not identified. Presumably, mercury escaped from contaminated pipes and other equipment which were replaced, in part, during modernization.

In assessing the significance of industrial effluents at Dryden on the receiving stream, we considered the effects of current mercury loadings, the effects of non-mercurial industrial wastes on methylmercury partitioning in the aquatic environment, and the effects of industrial wastes on the bioavailability of methylmercury in the aquatic environment.

During the study period the only effluent treatment for the total mill discharge was a small holding pond designed to eliminate foam from the river. Since November, 1980, effluents from the total complex have undergone primary treatment, and secondary treatment is expected to begin in 1983.

7.2 EFFECTS OF CURRENT MERCURY LOADINGS ON THE AQUATIC ENVIRONMENT

The production of methylmercury within the watercourse is much greater than the industrial loading. Some of the inorganic mercury released at Dryden will, however, be converted to methylmercury and, ultimately, will be taken up by sport fish. The following discussion compares the effects of current and historical discharges.

Table 7.2 compares daily mercury discharges at Dryden in 1975, before and after mercury cell removal, with daily data we collected in 1979 and 1981. The 1975 survey highlighted the potential problem of poor precision due to short-term fluctuations in mercury concentrations in industrial effluents. However, mercury concentrations obtained from daily, integrated samples provide better precision (Figure 7.1). The trend of decreasing mercury concentrations in the industrial effluent appears to have leveled off at about 10 kg per year. Industrial effent was usually sampled once a week. As a safeguard, there were several periods when samples were collected daily for 10 consecutive days. Primary treatment of the total industrial wastes began in September,

1980. In an special survey carried out between March 22 and April 1, 1982, primary treatment was found to remove 20-30 percent of the mercury in the total mill effluent (Romani, 1982).

Natural mercury loadings in the Wabigoon River at Dryden are 2-3 kg/y (kilograms per year). Thus, present anthropogenic mercury discharges at Dryden are about four times background loadings. Industrial releases are about the same as natural mercury loading to Clay Lake. The immediate effect of industrially released mercury is limited to the upper portion of the Wabigoon River. The random fluctuation in mercury loadings at Wainwright Dam compared to the strong, seasonal trends at Clay Lake suggests that mill discharges are not directly transmitted to Clay Lake.

A survey in October, 1982, when the mill was not operating, showed that there was mercury release from river sediments. There was apparently sufficient release to achieve a steady-state between mercury in sediment and water at the Wainwright Dam and sites downstream.

The form of mercury in the industrial effluent was studied in April and August, 1979, with a portable field centrifuge. The centrifuge did not remove all the particulate matter in the effluent and only about 67 percent of incoming particulate matter was recovered. The suspended solids were analysed for total mercury and several solvent extractable fractions (Table 7.3). More than 95 percent of the mercury on particulate matter was strongly bound and not readily exchangeable with other components of the environment.

Current mercury loadings from the plant will partition into various components of the receiving stream, as described in Sections 4 and 6. Under current conditions, loadings from the Dryden mill contribute little to the total source of mercury in Clay Lake. As old mercury deposits in the river are removed, present mercury loadings may be of more concern.

7.3 EFFECTS OF NON-MERCURIAL INDUSTRIAL WASTES ON METHYLMERCURY PARTITIONING

Non-mercurial industrial wastes discharged at Dryden have altered the aquatic environment in the receiving stream. Natural sediments in most of the Wabigoon River between Dryden and Clay Lake are covered with or contain organic debris from the mill. Changes in water chemistry caused by mill discharges have been found as far downstream as the English River confluence. Mercury cycling is probably affected by biogeochemical changes in the receiving stream and sediments as wastes introduced at Dryden are assimilated.

Some insights on the net effects of non-mercurial wastes on mercury cycling in the receiving stream, can be gained by examining the mercury cycle at selected sites under the lowest dilution of mill wastes. This situation occurred in the summer of 1980 when a 1:1 dilution ratio was recorded just downstream of Dryden. At this time, much of the river turned anoxic. Under these low flow conditions, methylmercury and total mercury levels were higher at most sites than during normal flows.

All available data suggest that the greatest effects of waste loadings on mercury cycling occur between Dryden and the eastern basin of Clay Lake. No effects could be detected in mercury concentrations in water at the outlet of Clay Lake.

7.4 EFFECTS OF INDUSTRIAL WASTES ON THE BIOAVAILABILITY OF METHYLMERCURY

The bioavailability of methylmercury in the eastern basin of Clay Lake was substantially reduced during the low flows in the summer of 1980 (Section 6). During this time, organic wastes introduced at Dryden were not completely oxidized by the time they reached Clay Lake, and there were substantial changes in water chemistry at this site in comparison to 1978 and 1979 (Ministry of the Environment, unpublished data). The specific cause of the reduced bioavailability of methylmercury is unknown, but may well be related to increased sulphide levels or some other component of mill wastes.

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TABLE 7.1. Annual mercury discharges from the chlor-alkali plant, Great Lakes Forest Products Limited, Dryden.

Year	Mercury Loss (kg)
1962-69	1100
1970	350
1971	9.1
1972	2.3
1973	2.1
1974	1.7
1975	2.0
1976	1.2
1977	1.7

TABLE 7.2. Total mercury loadings[a] from the industrial complex at Dryden during short-term surveys, 1975-1981.

1975		1979		1981	
Date	Loading (kg/day)	Date	Loading (kg/day)[d]	Date	Loading (kg/day)[e]
Jul 20	.139[b]	May 2	.076	Feb 25	.0068
21	.235	3	.041	26	.0091
22	.097	4	.037	27	.0054
23	.097	5	.044	28	.0091
24	.055	6	.019	Mar 1	.0054
25	.485	10	.041	2	.0086
Oct 9	.086[c]	11	.057	3	.0109
10	.064	12	.046	4	.0077
11	.087	13	.026	5	.0068
12	.071	14	.099	6	.0018
13	.060	15	.046		
14	.207	16	.026		
±	.140±.123		.047±.022		.0072±.0026
Range	.055-.485		.019-.099		.0018-.0109

[a] From the total industrial complex.

[b] From B. P. Neary (1975), Table 3, Calculation 1 (mercury cells in operation).

[c] From B. P. Neary (1976), Table 1, Calculation 3 (mercury cells removed).

[d] This study.

[e] Ontario Ministry of the Environment data, Northwestern Region.

TABLE 7.3. Solvent extractable fractions of mercury associated with particulate matter in the total effluent from Great Lakes Forest Products Limited, Dryden, April and August, 1979.[a]

	April 28	August 2
Total mercury concentration in particulate matter (μg/g)	.31±.14	.20±.06
% of total mercury extractable in:		
Acetic acid	0	1.05
Calcium chloride	0.24	0
Hydroxylamine hydrochloride/nitric acid	0.15	0
Oxalate	0.61	0
Hydrogen peroxide	0	0
Sodium hydroxide	0.30	2.75

[a] For methodology, see Jackson et al. (1981).

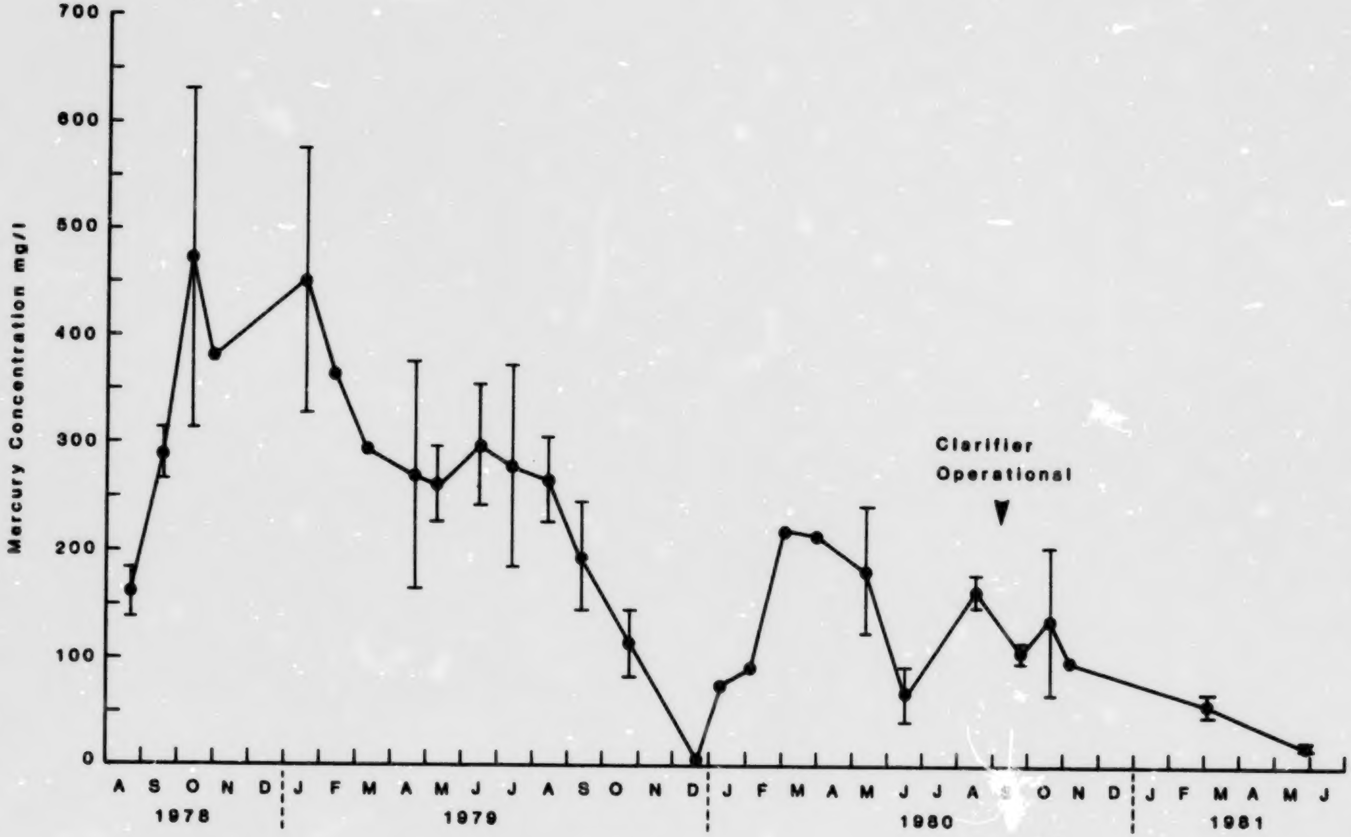

Figure 7.1 Mean monthly mercury concentrations of mill effluent, August, 1978–July, 1981.

8. REMEDIAL MEASURES

8.1 INTRODUCTION

Preceding sections of this report have outlined a basic understanding of mercury behavior in the Wabigoon/English River system. In this section of the report, we discuss possible remedial measures with regard to these findings. The key conclusions on the behavior and biogeochemical cycling of mercury within the contaminated portions of the river system are:

1. Elevated mercury levels in fish and other biota result from elevated mercury levels in surface sediments.
2. Mercury levels in biota are decreasing with time.
3. The principal factors governing mercury levels in biota are the concentration, speciation and physical form of methylmercury and, to a lesser extent, inorganic mercury in the water column.
4. During major portions of the year, total mercury and methylmercury levels in surficial bed sediments, water and suspended sediments come to "steady-state" (Section 4) within a few days.
5. Mercury levels in the water column are influenced by the feedback of mercury from local sediments, the influx of mercury released from upstream sediments, and the resuspension and transport of contaminated bed sediment by high flows. Recovery of the river system is thus inhibited by mercury release from local sediments and by mercury transported by the river from upstream.

The Federal study team investigated a variety of remedial measures which are not discussed here. These methods were designed to alleviate the mercury pollution problem without removing contaminated sediments. They included: (a) the addition of selenium to inhibit the formation and an uptake of methylmercury, (b) the addition of sulphide to sediments to reduce methylation rates and (c) the addition of phosphorus to increase productivity and 'dilute' bio-accumulated mercury through increased growth rates of fish and organisms in their diet. The reader is referred to the appropriate section of this joint report for further information. None of the foregoing methods has been recommended for implementation. The possible remedial measures which we discuss in this section of the report are:

- Dredging to remove and isolate contaminated sediment.
- Covering of contaminated sediments with clean material.
- Adding or resuspending clean sediment continuously.
- Flushing to transport, settle and isolate contaminated sediments.
- Mixing of contaminated and clean sediments.
- Diverting the river channel to isolate sediments in the most heavily contaminated parts of the Wabigoon River.

8.2 LEVELS OF MERCURY CONTAMINATION AND NATURAL RECOVERY RATES

Biological and chemical contamination of the Wabigoon/English/Winnipeg River system extends from Dryden to at least the Ontario-Manitoba border. The highest mercury levels were observed in the Wabigoon River system.

In Clay Lake, mercury levels in 1982 adult walleye and northern pike were about six times the mercury concentrations found in uncontaminated fish (Figures 5.11 and 5.12). Similarly, young northern pike (yearlings) in Clay Lake had mercury levels 6-12 times background concentrations (Figure 5.10). Adult and young northern pike and adult walleye from the lower English River system had at least twice the mercury expected in fish from uncontaminated waters. Mean annual methylmercury and total mercury levels in water showed geographical trends similar to those in fish (Tables 4.4 and 4.15).

Mercury levels in surface sediment of much of the Wabigoon River system were about two orders of magnitude greater than background levels (Figure 3.1). Concentrations were highest in sediments immediately downstream of Dryden where levels of 5-10 μg/g were common. In the most contaminated sediment layer in the English and Winnipeg Rivers, mercury concentrations were about 10 times background concentrations. Mercury levels in sediment decrease with distance downstream of Dryden more rapidly than do mercury levels in fish. This may result from transport of methylmercury from upstream and/or from changes in sediment and water chemistry as one proceeds downstream, leading to increased bioavailability of methylmercury as distance downstream of Dryden increases.

Continued contamination of the system is primarily the result of diffuse mercury sources in sediments throughout the river-lake system. Industrial discharges of mercury at Dryden are much less important than diffuse sources in retarding the recovery of Clay Lake (see Appendix 8 and Figure A8.5). As mercury levels in the system decline due to natural recovery (or remedial action), the significance of industrial sources to Clay Lake will tend to increase. We note, however, that there has also been a decline in the mercury loading from the mill complex. The industrial discharge of mercury during the study (August, 1978 - July, 1980) was 10-15 kg/yr. A more recent supplementary study (1982) showed that mill modernization and primary treatment of mill wastes had reduced this loading to 5-10 kg/yr. A further reduction may result from the recent installation of secondary treatment and other measures which are part of the modernization process.

Mercury levels in biota and sediment in the contaminated parts of the Wabigoon/English/Winnipeg River system have improved substantially since the early 1970's. Future improvements will likely proceed at a much slower rate. In the Wabigoon River system, substantial declines in mercury levels in adult walleye (approximately 10 years old) and adult northern pike (approximately 5 years old) are evident in Clay Lake (Figures 5.19 and 5.20). Crayfish, which have a much shorter life span and hence better represent temporal changes in mercury concentrations in the environment, show a clear exponential decline with relatively little change in the last several years (Figure 5.18).

Recovery of the English River system will not be a rapid process either. Mercury concentrations in adult walleye and northern pike will remain well above background levels for the foreseeable future, if no remedial measures are undertaken.

8.3 MERCURY CYCLING

8.3.1 MERCURY SOURCES AND LOSSES

The ability to describe the sediment-water behaviour of mercury during much of the year in steady-state terms has some important implications in determining the significance of present and future mercury sources. For the Wabigoon River, we have identified the major contributors of mercury to the water column under present conditions. These are the sediments in the vicinity of major influxes of clean water, such as the reaches downstream of Wabigoon Lake and the Eagle River confluence. Much of the mercury in the water column at the first monitoring sites downstream of Dryden (Wainwright Dam) may be derived from current industrial releases. If there are no major influxes of clean water into any given reach, our studies indicate that these reaches are not net contributors of mercury to the water column except under high flows when sediment resuspension occurs. These sediments do, however, retain the potential to contaminate overlying waters, should upstream sections be cleansed of mercury. The Wainwright Dam area, for example, was not identified as a mercury source during the study period, but results from a study in October, 1982 clearly show that sediments between Dryden and the outflow of the Wainwright Dam are capable of releasing significant quantities of mercury, if upstream loadings (mill discharges) are substantially reduced (MOE unpublished data). Thus, it is not sufficient to develop remedial measures based on present source loadings alone. Remedial measures must also take into account the potential of mercury enriched sediments to contaminate overlying waters and to be carried downstream.

Pathways for the removal of mercury from the various parts of the river system may include sedimentation, export through the water column, and loss to the atmosphere. The western basin of Clay Lake was identified as the only significant sink for total mercury. For methylmercury, no sinks were identified. From long-term biota trends, however, one can surmise that methylmercury concentrations in water are dropping with time. This applies to both lake and river sites.

The biota data suggest that methylmercury levels are not at true steady-state; there are presently small but ecologically important methylmercury losses in each part of the river system. Methylmercury and total mercury losses from each subsystem will continue until the system "re-equilibrates" with present mercury loadings from the industrial complex. The results of this study show that improvement has occurred fairly rapidly since mercury losses from the mill complex were sharply curtailed in 1970. They also suggest that the rate of improvement in future will be slower and that natural recovery of the system to acceptable levels will take several decades.

8.3.2 THE DISTRIBUTION OF MERCURY IN THE WABIGOON RIVER AND THE SIGNIFICANCE OF DIFFUSE AND POINT SOURCES

By combining steady-state concepts with mercury transport and biological data, one can gain a sense of how mercury moves through the river system. In certain cases, some perspective on the importance of various sources - existing and potential - on downstream reaches can be gained. This can be achieved by selecting a section of the system and treating all sediments in this reach as a point source for downstream systems.

For example, in the river reach between Dryden and the Wainwright Dam, we have concluded that sediments are not presently net contributors of mercury to the water column but are a potential long-term source. Let us assume that all anthropogenic point sources upstream of the Wainwright Dam inflow are eliminated. Also, assume that sediment-water partitioning is complete at the outflow; this is overly optimistic but will serve for purposes of this discussion. The large quantity of mercury behind the structure will then serve as a long-term source. Annual loadings will be dependent upon the quantity of mercury in the reservoir that can be mobilized either through high flow events (resuspending of bed sediments) or "solublization" to satisfy the sediment-water partition coefficient. Using long-term mean streamflows, mercury loadings from the Wainwright reservoir for the near future would be about 15 kg/yr. This mercury leaving the Wainwright reservoir would cycle through the water column to downstream sediments, much of it becoming part of the 1000 kg or so of mercury in the river between the dam and Clay Lake (Table 3.6). Although all of this 1,000 kg of mercury in the river is not ecologically active under current conditions, loadings from the Wainwright Dam likely have negligible effects on fish in Clay Lake. Contaminated sediments between the dam and Clay Lake are much more important than loadings from above the Wainwright Dam.

During the study, sediments between Dryden and Clay Lake were the source of approximately 20-25 kg/yr of anthropogenic total mercury for Clay Lake. Bottom sediments in Clay Lake contain the better part of 2,000 kg of anthropogenic mercury (Armstrong and Hamilton, 1973). Thus, one can conclude that as a result of the release of mercury from bottom sediments by sediment-water partitioning, the removal of anthropogenic mercury from sources upstream of Clay Lake would probably have limited effects in the short-term on conditions at the Clay Lake outflow. The short-term effects of this action on systems further downstream (i.e.: the English River system) would be further reduced due to additional diffuse sources in the river between Clay and Ball Lakes.

Much of the forgoing discussion is qualitative, and neglects possible sediment resuspension due to extremely high flows. Mercury form and bioavailability are also neglected. It should be noted, for example, that Clay Lake was effective in removing 30 to 50 percent of the total mercury which entered via the river, persumably by the settling of suspended material. Clay Lake, however, was not a net sink for methylmercury. Using similar assumptions, mathematical modelling can be used to compare the likely benefits of various remedial strategies. An example of a simple model is shown in Appendix 8. The results, however, must be used with caution unless the factors which have been neglected here can be taken into account.

8.4 THE ENVIRONMENTAL EFFECTS OF MOVING MERCURY CONTAMINATED SEDIMENTS

Remedial measures may deliberately or accidentally resuspend and translocate mercury-enriched sediments by implementation of measures such as flushing or dredging. It is, therefore, appropriate to examine the likely environmental effects.

Translocation of resuspended contaminated particulate matter must address two questions: the short-term effects of bioavailable mercury and methylmercury levels in water resulting from the sediment resuspension, and the long-term effects of this transported material on mercury cycling in the areas where it settles.

8.4.1 SHORT-TERM EFFECTS

Peddicord, et al. (1978) exposed two species of mussels (Mytilus edulis and Mytilus californus) and spot-tailed shrimp (Crangon nigromaculata) for three weeks to levels of suspended particulate matter containing 1,000 to 3,000 ng/ℓ of total mercury. There was no evidence of mercury accumulation in any of these organisms and, in fact, levels of mercury in mussels substantially decreased during some experiments. Tarao, et al., (1976) using resuspended mud from Minamata Bay to give total mercury levels up to about 40,000 ng/ℓ, recorded 80-100 percent increases in mercury concentrations in Red Sea bream (Figure 8.1) but the resulting concentrations were still quite low (less than 0.2 ppm). In a significant portion of a 63-day experiment with free-swimming pearl dace and fine-scaled dace, Rudd, et al. (1980) observed three- to four-fold increases in mercury levels in water resulting from bottom sediment resuspension. There was no significant change in mercury levels in fish.

Available data indicate, therefore, that during exposure of organisms to water containing high concentrations of total mercury in resuspended particulate matter major increases in mercury levels of the organisms do not occur. Since we have shown that most of the mercury in fish is in the methyl form, the examples just cited indicate that little methylmercury was formed despite the presence of large quantities of mercury in the water column, and/or that little of the methylmercury formed was available for bioaccumulation. Methylmercury was less than 0.2 ng/ℓ in all experimental water used in Tarao's study. Studies on sediment particulate (Jackson and Woychuk, 1980) and suspended sediment (Jackson, et al., 1983) revealed that about 95 percent of the mercury associated with these components was very strongly bound and was presumably not readily available for methylation (Figure 4.56). In view of these findings, Tarao's results are not surprising. Several investigations have revealed that when particulate matter is resuspended, the quantity of mercury desorbed is low (Ramamoorthy and Rust, 1976; Lindberg and Harriss, 1977; Muller and Schleichert, 1977). Lindberg and Harriss (1977) noted that, at steady-state, dissolved mercury levels in the water column were only elevated by a factor of two when sediment was resuspended at concentrations of 30,000 mg/ℓ and total mercury levels exceeded 8,000 ng/ℓ.

Other data in the literature agree with our findings for the Wabigoon River (Section 4) where, during high flows, total mercury levels rose but methylmercury concentrations showed little change. Furthermore, nearly all the methylmercury in river water during spring runoff was associated with particulate matter (Jackson, et al., 1983), and was presumably not nearly as bioavailable as dissolved methylmercury. Also, inorganic mercury from resuspended particulate matter in the water column in the spring runoff was unavailable for methylation (Figure 4.55). Although concentrations of suspended material and total mercury levels in the water would be much higher during deliberate flushing than during the spring runoff, the foregoing evidence suggests that soluble methylmercury levels in water would be only marginally elevated during sediment resuspension. Results from this study and results reported in the literature suggest that methylmercury levels in water are related to the soluble inorganic mercury fraction and that the short-term effects of resuspending mercury-enriched sediments on mercury levels in fish should be minimal.

8.4.2 LONG-TERM EFFECTS

The effects of transported sediment at its new site can be predicted as outlined in Section 6. The effects of the translocated sediment will not be adverse if the mercury level in the newly deposited material is less than or equal to the existing concentration in the substrate at the new site, assuming that the newly settled material and substrate are geochemically similar. The concentration of mercury in newly deposited material could be diluted by the addition of clean sediment. Any geochemical differences would have to be taken into account since geochemical characteristics are known to influence the release and partitioning of mercury. In Section 4, we suggest that methylmercury levels in water are probably negatively correlated with the organic content of bed sediment.

8.5 POSSIBLE REMEDIAL MEASURES

8.5.1 DREDGING

Contaminated sediments in the Wabigoon River upstream from Highway 105 contain 25-55 percent of the estimated total mercury loss of 9 tonnes from the chlor-alkali plant. The physical removal of these mercury-contaminated sediments would undoubtedly be an environmentally effective measure, eliminating mercury feedback and downstream transport. For a fluvial system, where sediments are subject to erosion and resuspension by high flows or extreme events, dredging may be the most effective and secure remedial measure.

The use of dredging to remove contaminated sediments from the Wabigoon River has been investigated by Acres Consulting Services during studies carried out for the Ontario Ministry of the Environment (Acres, 1982). This initiative was based on the Progress Report for the Federal/Provincial study of mercury pollution in the Wabigoon/English River system. That report concluded that contaminated sediments in the Wabigoon River above Clay Lake are a source of mercury to Clay Lake and waters further downstream; also, that remedial measures applied to Clay Lake alone would be of limited value if measures were not also taken to deal with this influx of mercury from the river.

The Acres' engineering report indicates that the removal of contaminated sediments from the Wabigoon River is feasible using small floating hydraulic dredges with mechanical cutterheads. In most parts of the river, the depth of the contaminated sediment layer is only a few centimetres. Some modification of existing cutterhead-and the depth-of-cut controls is necessary to ensure that excessive overdredging does not occur. The consultant noted that while in the past, dredging equipment has not been designed with a view to limiting turbidity or controlling depth of cut to the few centimetres required, more recent equipment now available is more suited to this type of work. The consultant also identified and selected sites adjacent to the river for the disposal and confinement of the mercury contaminated sediment removed by dredging. These sites are all located on Crown land remote from residential areas and offer an environmentally acceptable method of disposal. Sediments dredged from the river would be conveyed in the form of a slurry to the disposal areas via a floating and overland pipeline.

The cost of removing contaminated material from the 80 km reach of the Wabigoon River between Dryden and Clay Lake was estimated at $19 million (1981 dollars). This estimate includes the cost of dredging, the transport and disposal of contaminated sediment, the costs of temporary access for disposal-site development, and the covering and revegetation of the dewatered sites. It also includes a generous 50% contingency allowance, recognizing the somewhat unusual nature of the project and site conditions. Cost estimates are based on a program in which dredging would be limited to the ice-free season and would require a period of approximately 3 years for completion. Sediment data (Section 3, Figure 3.9) show that the most severely contaminated bed sediments are found in the upper reaches of the Wabigoon River with a sharp decline in mercury concentrations of sediment at the Highway 105 crossing. It is probably appropriate to limit dredging to the 62 km reach of the river between Dryden and Highway 105 to reduce costs. This would reduce the total quantity of material requiring removal and confinement by approximately 13 percent. Modelling studies (MacKay and Paterson, 1983) also suggest that the recovery of Clay Lake would benefit most from the removal of contaminated sediments from the upper reaches of the river between Dryden and the Eagle River confluence.

The major benefits of dredging as a remedial option include:

- The removal and confinement of the mercury-contaminated sediments can be carried out with a high degree of control and confidence in its effective implementation.
- Loss of contaminated sediment during dredging would be minimized by the techniques selected and most of the disturbed material would resettle in the river. For this reason, dredging should start at Dryden so that disturbed sediment is removed as dredging progresses downstream. It is anticipated, therefore, that there would be little or no environmental impact on Clay Lake due to disturbance of contaminated sediments.
- The use of proven technology and equipment (with some modification) provides a sound basis for, and gives confidence in, cost estimates.
- The risk of unforeseen environmental consequences is very low. The technique permanently removes the mercury from the river system eliminating possible future disturbance and downstream transport.
- Much of the river bed between Dryden and the Eagle River confluence is presently covered by organic wastes from past pulp and paper operations. These organic wastes, which cause oxygen depletion and inhospitable conditions for most aquatic organisms, would also be removed by dredging.

8.5.2 COVERING CONTAMINATED SEDIMENTS

The natural recovery of the river system which is occurring at present may be attributed mainly to three processes: (a) the burying and dilution of contaminated sediment by natural sedimentation, (b) export of mercury by downstream transport, and (c) loss of mercury to the atmosphere. To reduce the transfer of mercury from contaminated sediments to overlying water, contaminated sediments could be covered with clean material. This may be viewed as similar to accelerating the natural sedimentation process. The method is most applicable to lakes where bottom sediments are not susceptible to erosion and disturbance except in shallow areas affected by wave action. In a river, the technique would be less satisfactory, because erosion during high flows would likely cause re-exposure of contaminated sediments. In Clay Lake, sediment disturbance would likely be limited to the effects of wave action in shallow areas (notably the Eastern Basin), and to disturbance by bottom-dwelling organisms and gas bubbles generated by the decay of organic matter. The relationships between mercury concentrations in sediments and mercury concentrations in overlying waters established by this study incidate, however, that the covering material need not provide a complete seal for the method to be effective. Mercury feedback would be significantly reduced by the very substantial lowering of mercury concentrations in bed sediment at the sediment/water interface. The effectiveness and permanence of this approach would, of course, be reduced unless measures are first taken to deal with the mercury contaminated sediments in the Wabigoon River above Clay Lake. These sediments release mercury and methylmercury to overlying waters and are susceptible to erosion and downstream transport during high flows; thus, mercury enters Clay Lake with the inflow from the river.

There is some difficulty in estimating the optimum thickness of the layer of clean cover. Sediment disturbance by bottom-dwelling organisms (bioturbation) generally extend to a depth of about 5 cm in Clay Lake. This is, perhaps, the optimum thickness of cover but we believe that 2 or 3 cm would significantly reduce mercury feedback and accelerate recovery. The use of clean clay or sediment to cover contaminated sediments in Clay Lake was investigated briefly by Acres. The consultant concluded that this could probably be accomplished most economically by using a hydraulic dredge to mine clean sediment from beneath the mercury-contaminated layer of bed sediments in Clay Lake. Coring is necessary to confirm the presence of adequate supplies of suitable material. A floating pipeline would be used to place the material to obtain a reasonably uniform thickness of cover. It may alternatively be possible to use terrestrial deposits adjacent to the lake. Acres estimated that placing a cover of clean material would cost $0.9 million per centimetre, if undertaken as an additional measure after capitalizing much of the necessary equipment for the removal of contaminated river sediment by dredging. This translates to a total cost of between $1.8 million and $2.7 million (1981 dollars) for a 2 or 3 cm coating. During an operation of this type, some clean clay or sediment would escape and settle in the Wabigoon River system in areas downstream from Clay Lake. This would be beneficial in reducing mercury feedback from contaminated sediments in those areas. If the costs are acceptable, the technique could also be applied directly to other areas in the Wabigoon/English River system to further accelerate recovery.

8.5.3 CONTINUOUS ADDITION OR RESUSPENSION OF CLEAN SEDIMENT

It may be considered that there are two factors retarding recovery of any site in the contaminated parts of the Wabigoon/English River system. Mercury feedback from contaminated sediments in the immediate area is one factor. The influx of mercury to the site from upstream sources (feedback from upstream bed sediments and resuspension and transport of contaminated sediment) is the other. Removal or covering of contaminated sediments may address these factors. There may, however, be another approach for dealing with the influx of mercury from upstream. Work done by the Federal study team in enclosures in Clay Lake (Rudd, et al., 1983) indicates that suspended sediment concentrations of approximately 17 mg/ℓ inhibit mercury uptake by fish. Sediments from Clay Lake were effective in inhibiting mercury uptake but some river bank deposits were ineffective. This suggests that the bio-availability of mercury in the water column could be inhibited or reduced by the continuous addition of clean sediment. For maximum effect, continuous round-the-clock addition of clean material during all seasons would be necessary. It may, however, be effective to limit the operation to ice-free seasons because warm-water sportfish accumulate 80 to 90 percent of their mercury bodyburden at that time of the year (Norstrom, et al., 1976; Colby, et al., 1979). This semi-continuous addition and suspension of clean material would have to continue for several years, since upstream sources will remain active for decades unless they are removed or covered. The addition of clean material will also accelerate recovery by reducing feedback from contaminated sediments in areas where it settles. Field trials are necessary to confirm the technical feasibility of this technique as a remedial measure and to develop cost estimates for its use. These trials would need to establish:

1. The minimum or optimum concentration of suspended sediment necessary to inhibit biological uptake of mercury and the type of material which is most effective. The work done by Acres on flushing showed that the size range of contaminated sediments from the Wabigoon River presents serious difficulties for using the river to carry sediment. If clean sediments exhibit a similar size grading, a major build up of material close to the point of addition would occur through the settling of the larger size fractions. This problem would have to be addressed and may favour the use of selected clay deposits, if they are available at appropriate locations.

2. The type of equipment needed for the aquisition and mechanical dispersion of the sediment or clay.

3. The number of sites at which clean sediment additions have to be made to significantly accelerate recovery of the system.

4. The number of years for which treatment is to be applied. This is necessary to establish overall costs for use of this technique. The information already presented on the natural rate of recovery of the system suggests that treatment would have to continue for many years; perhaps decades.

5. The environmental acceptability of these continuous sediment additions.

If the technique proved technically feasible and economic, it could be used to inhibit mercury uptake in selected areas of the Wabigoon/English River system. The method might first be applied to nullify or reduce the impact of mercury entering the English River from the Wabigoon River, thus accelerating the recovery of the English

River system. If field trials for this method are made prior to the implementation of other remedial measures, it would be advisable to conduct the trials in areas below the inflow to Clay Lake. Otherwise, the possible application of other remedial measures to the Wabigoon River between Dryden and Clay Lake may be jeopardized or complicated.

8.5.4 FLUSHING

The purpose of flushing is to remove mercury-enriched sediments from the river by resuspending them and using the river flows to transport them to settling and disposal areas adjacent to the river. As an alternative, contaminated sediments could perhaps be flushed into temporary settling areas for subsequent removal and disposal. A third possibility is to flush sediments downstream to a lake where they would settle in areas less subject to sediment erosion and resuspension. This would accelerate a natural process now occurring in the Wabigoon River. The feasibility of flushing depends on several factors including relationships between mercury concentration and particle size, the particle-size distributions of contaminated sediments, river channel capacities, and flows available for flushing by flow regulation.

The feasibility of flushing was also investigated by Acres Consulting Services Limited (Acres, 1982). The consultant concluded that the size range of particles in contaminated sediments in the Wabigoon River between Dryden and Clay Lake presents serious difficulties. These include:

1. Bank-full river flows and mechanical resuspension would be necessary to mobilize the larger size fractions of the contaminated sediments. This situation requires the use of very large settling areas for settling the smaller sediment particles. The sediment-trapping efficiency of Clay Lake was estimated at 90 percent.
2. Monitoring during execution would be difficult. The process would also be difficult to control with a danger of dispersion of mercury contaminated sediment into areas adjacent to the river and to waters downstream from Clay Lake.
3. The need for mechanical resuspension escalates costs, which were estimated to be in the range of $10-$20 million.
4. The limited water supply available in the river system would limit the flushing operation to a period of approximately 25 days per year, and would extend the flushing operation over a period of about 6 years.

The ability of the river channel to carry the flows needed to transport suspended sediment during flushing and to reduce its premature settling could perhaps be improved by increasing the channel gradient. This possibility was not investigated by Acres and has not been studied in detail. Preliminary field study suggests that increasing channel gradient by cutting through rock outcrops at selected sites is feasible (Figure 8.2). An increased gradient might provide the energy to erode substantial quantities of contaminated sediment and clean material during spring runoff or high flows generated by flow regulation. Most of the sediment eroded and suspended in this way would settle in Clay Lake. Construction of a dam at the outlet of Clay Lake might increase the lake's efficiency from 90 percent under present conditions to about 95 percent; however, this measure would further escalate the cost of the technique.

Even with gradient modification, flushing may not be effective without mechanical resuspension. Furthermore, it might release unacceptable quantities of mercury contaminated sediment to Clay Lake and beyond. Certainly, the process would be difficult to control and the efficiency and environmental effects difficult to forecast. For the reasons outlined, further consideration of flushing is not recommended.

8.5.5 MIXING CONTAMINATED AND CLEAN SEDIMENT

Because mercury-enriched sediments in most of the system are restricted to a few centimetres near the surface, substantial improvement could be obtained by mixing the surface sediment and the deeper, clean substrate together. The effectiveness of this technique would depend on the resulting concentration in the surface sediment layer, which is active in mercury release to overlying waters, and the amount by which this concentration would be reduced. The necessary mixing of sediments could perhaps be achieved by drawing a specially designed plough over contaminated sediments but the necessary mixing could be difficult to achieve and control, especially in deep waters. The method would also cause some resuspension and dispersion of contaminated sediment, which may cause unacceptable downstream transport of contaminated material, especially in a fluvial environment. The method has not been investigated in detail because of these disadvantages.

8.5.6 RIVER CHANNEL DIVERSION

Brief consideration was given to diversion of parts or all of the Wabigoon River above Clay Lake with the aim of isolating mercury contaminated sediments and organic matter in the existing river channel.

Unacceptably high concentrations of mercury in bottom sediments are found in most of the 80 km or so of river channel between Dryden and Clay Lake. From a practical standpoint, diversion of the Wabigoon River to bypass this most heavily contaminated part of the present river bed could extend, at most, from Wabigoon Lake to the Eagle River confluence, a distance of approximately 50 km. It is estimated that construction of the diversion channel alone would cost well in excess of $20 million. There would also be "hidden" costs and technical obstacles to such a scheme. The greatest difficulties would probably be associated with isolating the existing river channel and providing satisfactory handling of inflowing streams and local drainage. Due to these technical difficulties and the anticipated high cost, the method has not been investigated in detail.

8.6 RECOMMENDATIONS

Waste discharges from the former chlor-alkali plant associated with the pulp and paper-making industry at Dryden have contaminated major portions of the Wabigoon and lower English Rivers. This system of lakes and rivers is, consequently, one of the most severely mercury-polluted waterways in the world. The decline of mercury levels in fish has been fairly rapid since mercury discharges were severely curtailed in 1970. However, the results of this study indicate that natural recovery to acceptable levels in much of the river system will likely take several decades. The study also makes it clear that there are no complete remedies or easy solutions to the pollution problem. We believe, nonetheless, that the recovery of the system could be subtantially accelerated and mercury levels in fish reduced by selected remedial measures. We urge the Steering Committee, in formulating its recommendations to the Governments of Canada and Ontario, to give careful consideration to three measures discussed in this report. These measures are:

1. Removal by dredging of contaminated sediments from the 62 km reach of the Wabigoon River between Dryden and the Highway 105 crossing, and confinement of these contaminated sediments in disposal areas close to the river.
2. The covering of contaminated sediments in Clay Lake with clean clay or sediment to reduce mercury feedback.
3. The semi-continuous addition of clean sediment to the water column at selected sites in the river system following field trials to confirm the economic and technical feasibility of the method.

It may be appropriate to use more than one of these remedial techniques. The measures should be selected and applied to avoid interference with other measures and to avoid recontamination of areas already cleaned or treated. Cost-benefit analysis may aid decisions on the possible implementation of remedial measures.

For the Wabigoon River above Clay Lake, the best approach is the physical removal of contaminated sediment. Operations should start at Dryden and progress downstream to avoid possible recontamination of areas already restored.

River dredging alone would not be sufficient to restore Clay Lake but would substantially accelerate its recovery. To secure a rapid reduction in mercury levels in Clay Lake fish, the internal cycling of mercury from bed sediment within the lake must also be reduced or stopped. This could be achieved directly be placing clean material over contaminated sediment in the lake. It could alternatively be accomplished by suspending clean clay or sediment in the Wabigoon River at the inlet to Clay Lake for subsequent settling in the lake.

Mercury feedback from contaminated sediment of the upper Wabigoon River and Clay Lake, which jointly contain 47-77 percent of the estimated total quantity of mercury lost from the chlor-alkali plant, would be eliminated or reduced by these measures (dredging the river and covering sediments in Clay Lake). This action would also accelerate recovery of the English River and benefits would accrue fairly rapidly in the vicinity of Ball Lake.

In the sections of the English River distant from Ball Lake, the release of mercury from local sediments is more important than the influx of anthropogenic mercury from the Wabigoon River system. Response to measures applied to the Wabigoon River would, consequently, be limited and slow. To reduce mercury feedback and to effect speedy recovery of the lower English River in areas distant from Ball Lake, it is, therefore, necessary to reduce mercury levels in local sediments. This objective could be achieved directly by placing clean cover material over contaminated sediments or indirectly by suspending clean clay in the water column for subsequent settling. It may also be possible to use the semi-continuous resuspension of clean clay at selected sites in the English River to intercept the influx of mercury from upstream and substantially reduce the bio-availability of mercury in the water column.

In the Winnipeg River, mercury contamination is approaching normal levels and remedial action is not required.

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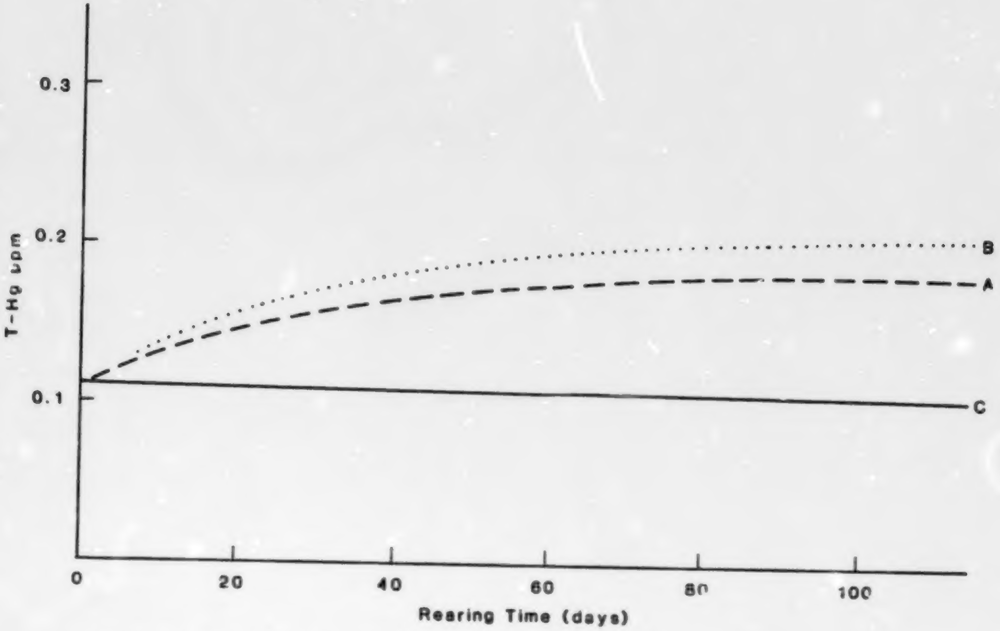
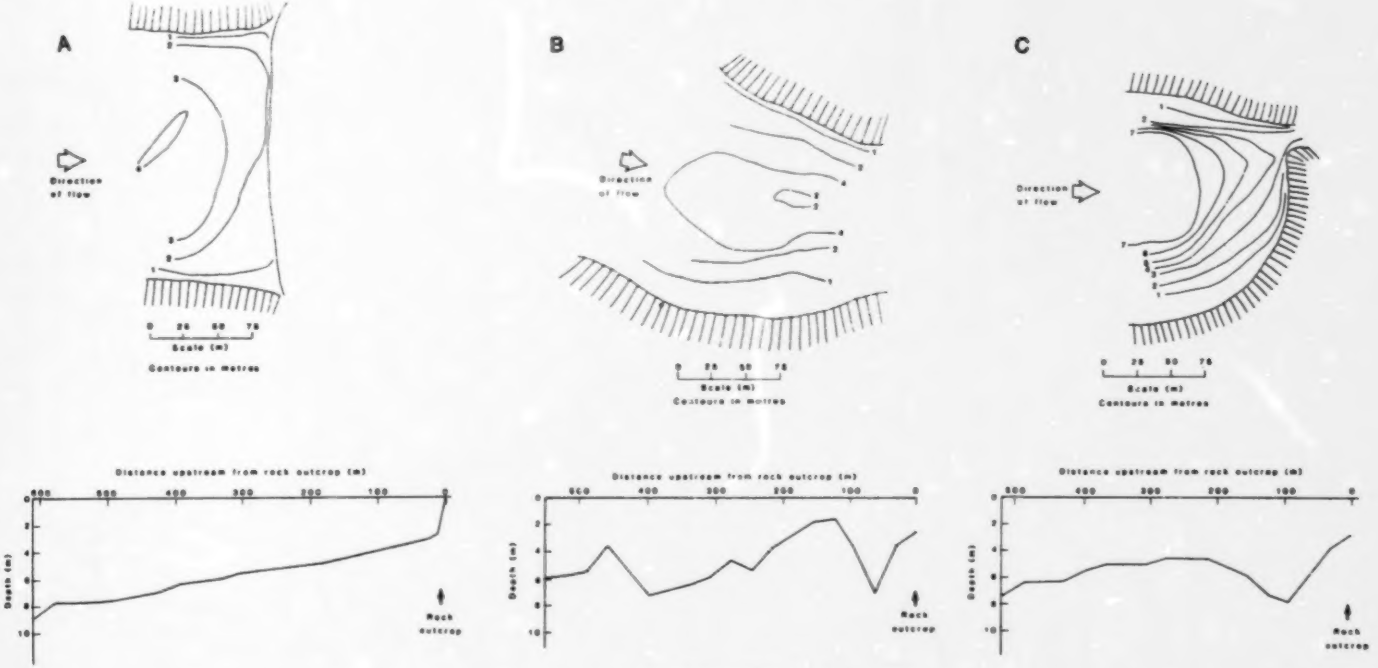


Figure 8.1 Total mercury concentrations in red sea bream reared in different environments.

A 40,000 ng/l Hg
B 6,000 ng/l Hg
C 200-300 ng/l Hg



Lateral and longitudinal river basin profiles, Wabigoon River–approximately 10 km downstream of the Eagle River confluence

Lateral and Longitudinal river basin profiles, Wabigoon River at Red Lake Highway # 105

Lateral and longitudinal river basin profiles, Wabigoon River at Quibell

Figure 8.2 Wabigoon profiles at three bedrock sills.

APPENDIX 8

A SIMPLE MATHEMATICAL MODEL OF MERCURY CYCLING

To determine expected changes in the Wabigoon River system with time, a simple mass balance of mercury cycling was calculated. The model selected is applicable to both lake and river systems, and its components are shown in Figure A8-1. Using the terms listed in Figure A8-1, the change in the concentration of surface sediment, C_{SA}, is proportional to waterborne mercury deposited in the surface sediment, J_{RSa}. J_{RSa} represents the difference between waterborne mercury entering and leaving the subsystem, less any loss to atmosphere ($J_{RSa} = J_{in} - (J_{out} + J_A)$). Since J_A has not been measured and is assumed to be zero, then $J_{RSa} = J_{in} - J_{out}$. If mercury entering the subsystem is at normal background levels, and if the sediment in the subsystem is contaminated, the J_{out} will exceed J_{in}. J_{out} may be calculated as the difference between waterborne mercury in the subsystem (C_w) and waterborne mercury entering the subsystem (C_{wi}), multiplied by the flow rate, Q. Thus, $J_{out} = (C_w - C_{wi})\ Q$. Because C_w is proportional to the degree of sediment contamination, mercury losses through the water will be greatest from the most highly contaminated subsystem, and water flowing over highly contaminated sediments will carry this contamination downstream. Thus, some of the anthropogenic mercury introduced at Dryden may cycle down the rest of the river system. How far downstream this cycling proceeds will depend upon flow and sedimentation rates, degree of mercury contamination in the next ecosystem downstream, losses from sediments to water, and on losses from water to the atmosphere.

A. THE PREDICTED LONG-TERM EFFECTS OF CURRENT INDUSTRIAL RELEASES ON MERCURY LEVELS IN FISH AT THE INFLOW TO CLAY LAKE

The model was applied to the Wabigoon River between Dryden and Clay Lake. The following assumptions applied to this application of the model.

(a) The relationship between total mercury concentrations in fish and in water is linear. An advantage in using total mercury instead of methylmercury is the better data base resulting from the lower analytical costs for the former. We chose 1+ pike for this example, but any species could be substituted providing that a relationship between its size and mercury level has been established.

(b) For specific sites, the relationship between declining mercury levels (due to recovery of the system) in water and in pike is linear. The point at the upper end of the regression in Figure A8-2 represents current conditions, and the point at the lower end represents conditions that are expected when all anthropogenic mercury leaves the system. Data for the latter point were obtained by assuming that uncontaminated conditions in the river would be similar to those at the two nearest control sites, Wabigoon Lake and Eagle River.

(c) Net loss to the atmosphere is zero.

(d) Annual net sedimentation rate is nil.

(e) For specific sites, the relationship between declining mercury levels in sediment and in water is linear (Figure A8-3).

(f) Mercury leaves the ecosystem only through the water column. For simplicity, waterborne mercury leaving the system was based on mean annual concentrations.

(g) The active sediment layer, S_A, is homogeneously mixed, is about 5 cm in depth, and does not interact with deeper sediment.

(h) Partitioning of mercury between sediment and water is complete at the inflow to Clay Lake.

(i) Mercury loadings from the industrial source at Dryden become part of a diffuse source to Clay Lake and slowly move downstream. The industrial discharge was assumed to be 2.5 kg of mercury per year. This value is based on the declining trend in mill loadings shown in Figure 7.1. We also assume that this mercury leaves the system in the year it is discharged.

(j) The effects of the chemical form of mercury are adequately reflected by use of site-specific relationships between mercury in sediments, water and biota.

The calculation was performed as follows:

$$\Delta C_s = \frac{M_{t=i}Hg - M_{t=i+1}Hg,}{\text{Mass of sediment}}$$

WHERE: ΔC_s = Change in concentration of total mercury in surface sediment in Wabigoon River at the inflow of Clay Lake. A value of 5 μg/g was assumed for time zero.

$M_{t=i}Hg$ = Mass of total mercury in surface sediment at time "i". At time zero, mass = 2020 kg.

$M_{t=1}Hg$ = Mass of total mercury in surface sediment one year later than time "i", = J_{out}.

J_{out} = $C_wQ-(C_{wi}Q + K_{pd})$

C_w = 5 ng/ℓ

Q = 49.1 m³/s

K_{pd} = industrial mercury discharge = 2.5 kg/y

$$C_s = \frac{C_w - 4.94}{3.65} \text{ (Figure A8-3)}$$

The predicted mercury concentration decreases in fish are shown in Figure A8-4. According to the model, many decades will be required to significantly reduce mercury levels to acceptable levels. Furthermore, the model excluded sediment below a 5 cm depth. If extreme floods exposed formerly inactive contaminated sediment, improvement would be further delayed. Spring floods are known to scour bed sediments in the upper portion of the Wabigoon River. Much of this material settles out in the river, upstream of Clay Lake, but may be subject to later resuspension. There may be significant losses to the atmosphere and the assumption of zero sedimentation rate is probably untrue for some parts of the river. The calculated results may be pessimistic. The value of the model lies primarily in indicating the relative significance of continued industrial loadings of 2.5 kg/yr versus historical deposits. Industrial discharges of mercury at Dryden presently have little effect on the predicted recovery rate of Clay Lake or areas farther downstream. Historical contamination is the main problem. As mercury levels in the river system decline, the significance of industrial sources will increase if they remain at present levels.

B. THE EFFECT OF INCREASING SEDIMENTATION RATES ON THE RATE OF RECOVERY OF CLAY LAKE

We also used the model to predict the change in mercury concentrations in fish to Clay Lake if all anthropogenic mercury upstream was removed. If no mercury is lost to atmosphere, then anthropogenic mercury is removed only by water transport from Clay Lake or by the burial of ecologically-active sediment with inactive, clean sediment. Although comprising two or more major sub-basins, the lake was modelled as a single entity. Partitioning of mercury in the lake was assumed to be complete, and the active sediment layer homogeniously mixed (Robbins and Edgington, 1975, 1976; Robbins, et al., 1979, cited from Fisher, et al., 1980). We also assumed that all the mercury leaving Clay Lake was cycled through Clay Lake sediments. Radiochemical experiments conducted by Rudd, et al., (1980) showed that the half-life of radiolabelled mercury in the water column in Clay Lake was 18-20 days. Hesslein, et al., 1980, found a half-life of 14.3 days for mercury in the epilimnion of a small shield lake. Since these values were considerably below the theoretical mean residence time of Clay Lake (57 days), our assumption is probably satisfactory. These assumptions and residence times suggest that less than 6-12 percent of the mercury entering the lake with the Wabigoon River inflow leaves the lake without being cycled through lake bottom sediment. We assumed a linear relationship between declining mercury concentrations in sediment and water (Figure 8.5), between declining mercury levels in water and suspended sediment, and between declining mercury levels in water and pike (Figure A8-6). The results of the model, for several sedimentation rates, are illustrated in Figure 8.7.

C. CONFIDENCE IN MODEL RESULTS

Some of the assumptions made for application of the model reflect the fact that satisfactory data on some of the processes involved are not available. The relative significance of some of the processes is uncertain. For these reasons, the model's quantitative usefulness is very limited and the results obtained must be used with caution. The major sources of inaccuracy probably are: (a) The assumption that the relationship between declining mercury levels in sediment and water is linear. (b) The depth of the active sediment zone probably varies from site to site. (c) Mercury losses to the atmosphere may be significant. (d) A small, possibly significant portion of the mercury in the water column has not been cycled through bed sediments. (e) Mean annual conditions may inadequately reflect season effects and the influence of extreme hydrological events on mercury transport. (f) The net sedimentation rate in many parts of the river system is not zero. (g) There is large variance in several of the relationships used in the model.

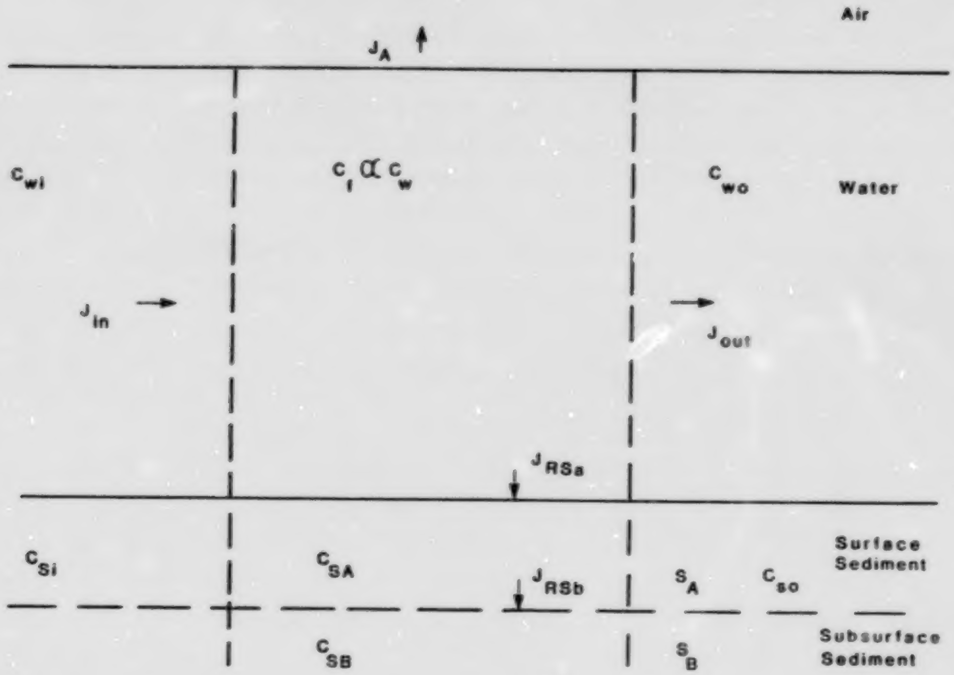

Air
J_A
C_{wi}
$C_f \alpha C_w$
C_{wo}
Water
J_{in}
J_{out}
J_{RSa}
C_{Si}
C_{SA}
J_{RSb}
S_A
C_{so}
Surface Sediment
C_{SB}
S_B
Subsurface Sediment

Figure 8.A1 A schematic model for mercury cycling in the Wabigoon/English/Winnipeg River system.

J_A=net mercury loss to atmosphere
J_{in} = waterborne mercury entering subsystem
J_{out} = waterborne mercury leaving subsystem
J_{RSa} = mercury into surface sediment
J_{RSb} = mercury leaving active surface sediment to inactive deeper sediment
S_A=active surface sediment
S_B=inactive subsurface sediment
C_w=level of total mercury in water in subsystem
C_{wi}= level of total mercury in water upstream of subsystem
C_{wo}=level of total mercury in water downstream of subsystem
C_{SA} = level of total mercury in active surface sediment
C_{SB} = level of total mercury in inactive subsurface sediment
C_{Si} = level of total mercury in surface sediment upstream of subsystem
C_{So} = level of total mercury in surface sediment downstream of subsystem
C_f = level of total mercury in fish

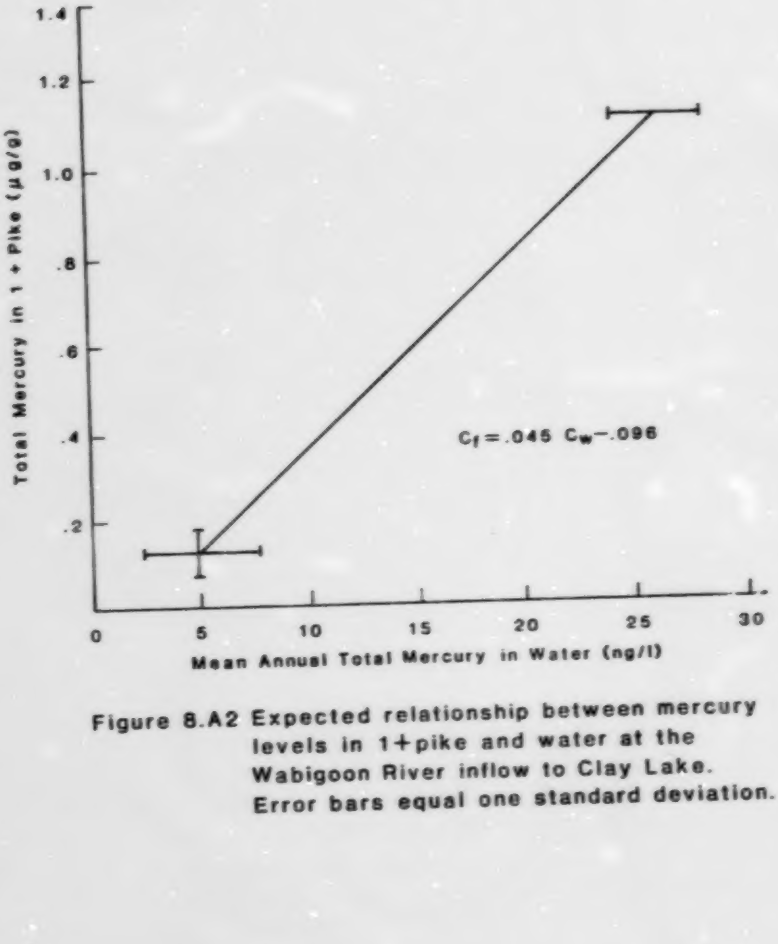


Figure 8.A2 Expected relationship between mercury levels in 1+pike and water at the Wabigoon River inflow to Clay Lake. Error bars equal one standard deviation.

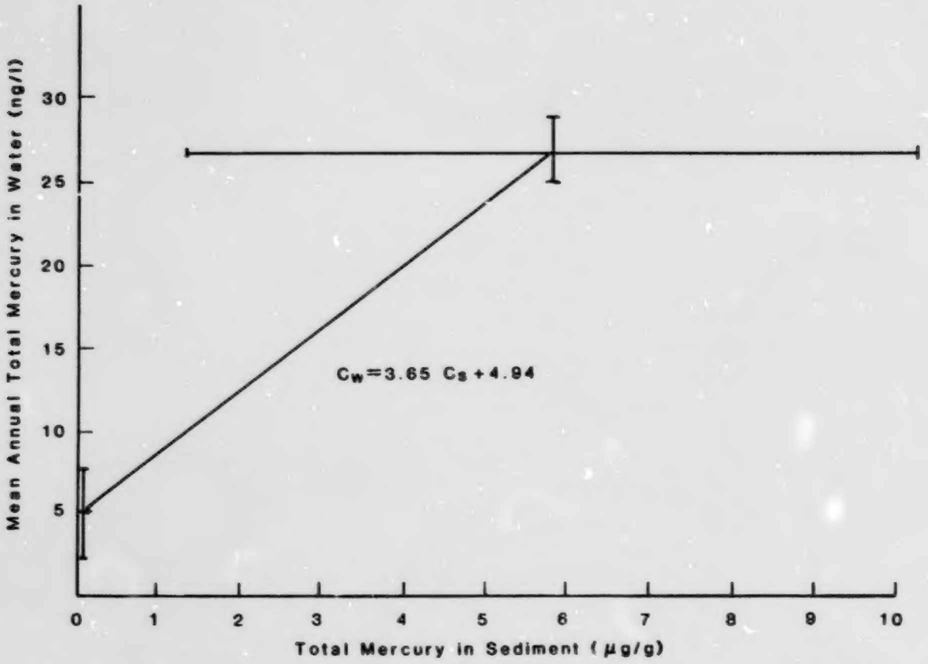


Figure 8.A3 Expected relationship between mean annual total mercury concentrations in water and mean total mercury concentrations in sediments in the Wabigoon River, Dryden to Clay Lake. Error bars indicate one standard deviation.

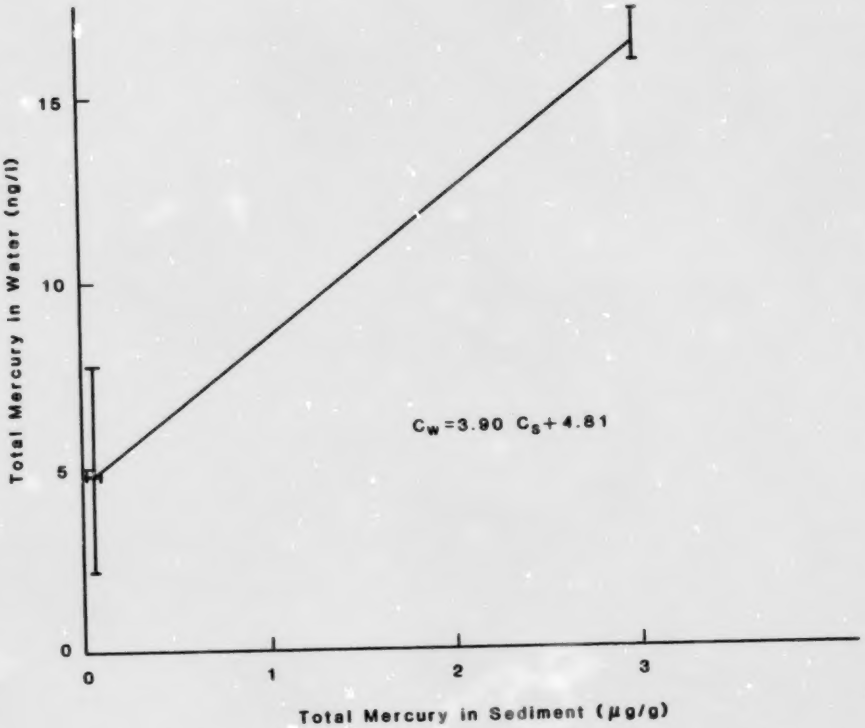


Figure 8.A4 Expected relationship between mean annual total mercury concentrations in water and mean mercury concentrations in sediment. (Error bars show one standard deviation. Data for clean sediment from sub-surface sediment in Clay Lake. Data for contaminated sediment from surface sediment in Clay Lake. Water data from mean whole-lake concentrations in Clay Lake).

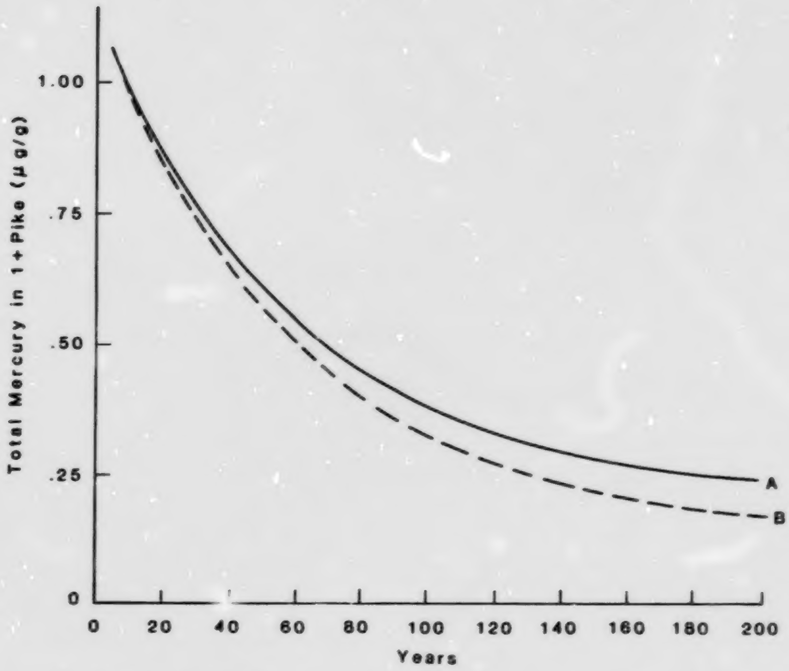


Figure 8.A5 Predicted mercury concentrations in 1+ pike at the inflow to Clay Lake under (A) continous industrial mercury loadings of 2.5 kg/year and (B) no industrial loadings. See text for conditions of model.

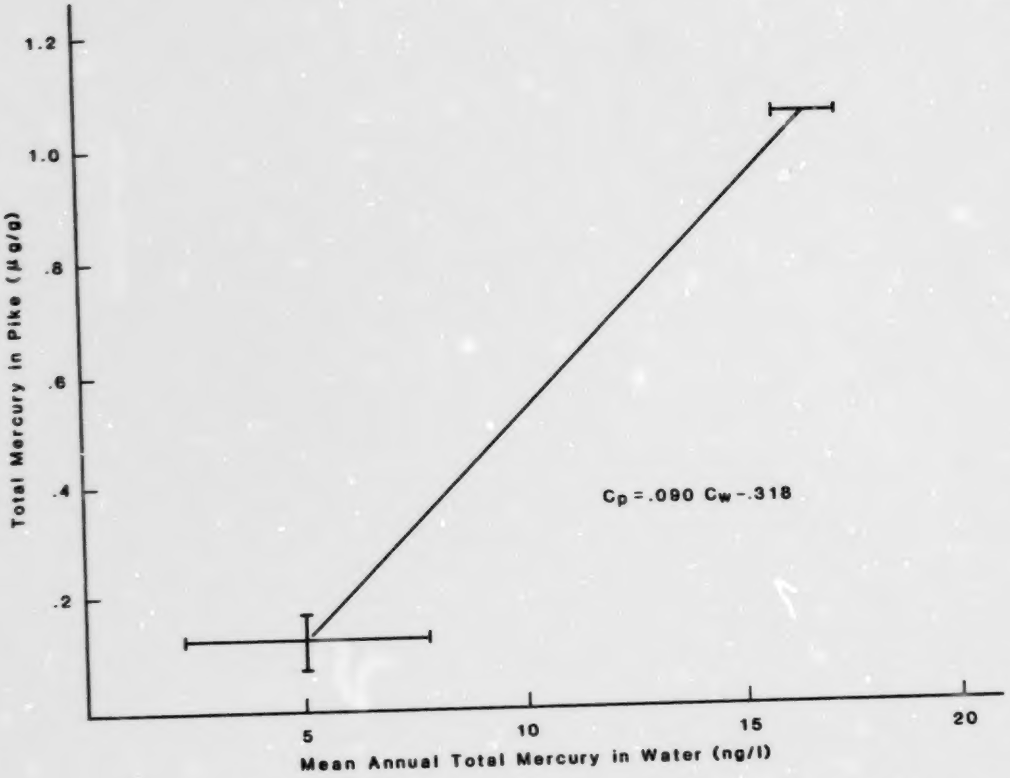


Figure 8.A6 Expected relationship between mercury levels in 1+pike and water in Clay Lake. Error bars equal one standard deviation.

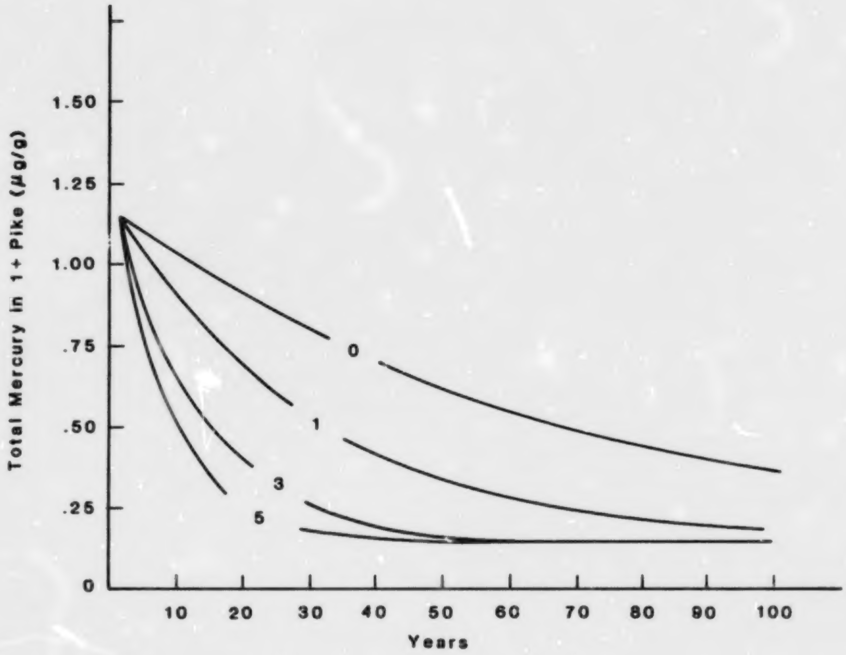


Figure 8.A7 Predicted mercury concentrations in 1+ pike in Clay Lake for sedimentation rates of 0, 1, 3 and 5 mm/yr . See text for conditions of model.

B. MERCURY POLLUTION IN THE WABIGOON-ENGLISH RIVER SYSTEM

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ACKNOWLEDGEMENTS

Our research into the mercury contamination of the English-Wabigoon River system benefitted from frequent worthwhile interchanges with several of our colleagues at the Freshwater Institute. This group included F.A.J. Armstrong, A. Lutz, D.W. Schindler, R.E. Hecky, D. Bodaly, R.D. Hamilton, G.J. Brunskill, S.G. Lawrence, R.H. Hesslein, P. Campbell, M. Gordon, M. Stainton, R. Schade and S. Elliot. A. Lutz, K. Supeene and C. Tamm, among others, analyzed many total and methyl mercury samples which provided us with a framework for the interpretation of our enclosure experiments. R.H. Hesslein, P. Wilkinson, E. Burns-Flett and E. Slavicek generously provided needed expertise in gamma isotope counting methodologies.

B. Lamm and G. Clark provided us with valuable field support and a greater understanding of the English-Wabigoon system.

Several others were also important sources of constructive criticism: these included A.L. Hamilton, J.W. Parks, T.A. Jackson, G. Mills, R. Allan, T. Brydges, K. Shikazi and D. Dodge. This work was funded by the Department of Fisheries and Oceans, the Department of the Environment (Inland Waters Directorate) and the Ontario Ministry of the Environment.

DISSOLVED AND SUSPENDED MERCURY SPECIES IN THE WABIGOON RIVER (ONTARIO CANADA): SEASONAL AND REGIONAL VARIATIONS

by

T.A. Jackson, J.W. Parks, P.D. Jones, R.N. Woychuk, J.A. Sutton and J.D. Hollinger

ABSTRACT

Seasonal and regional variations in the speciation, sediment-water partitioning, and dynamics of mercury (Hg) were studied at selected sites along the Hg-polluted Wabigoon River, and at unpolluted headwater and tributary sites, during April-September, 1979. "Dissolved" and "particulate" forms of Hg in the water were separated by continuous-flow centrifugation in the field. The Hg and other pollutants such as wood chips and salt had been discharged from the chlor-alkali plant and paper mill at Dryden, Ontario.

Concentrations and loadings of particulate methyl mercury (CH_3Hg^+) and total particulate Hg (and loadings of total "dissolved" Hg) were greatest during the spring flood (April-May) owing to accelerated resuspension and transport of sediments. Concentrations of "dissolved" CH_3Hg^+, however, were highest in the summer (July-September), probably reflecting stimulation of microbial methylating activity by elevated temperatures, together with factors such as reduced levels of metal-scavenging particulates and minimal dilution by runoff. Total dissolved Hg concentrations were relatively high in September at polluted sites only, possibly because of desorption from sediments due to elevated concentrations of Cl^- ions. Loadings of dissolved CH_3Hg^+ tended to be high in the summer but were generally depressed (suggesting sorption by suspended particles) during the major spring-flood episode in May.

During July-August dissolved CH_3Hg^+ was a function of total dissolved Hg, suggesting rapid biomethylation of desorbed inorganic Hg; but in general dissolved and suspended CH_3Hg^+ levels depended on environmental variables and were unrelated to total Hg concentrations. In the summer only, total dissolved Hg was a function of dissolved Cl^-. Hg species in particlates were associated with sulfides, hydrated Fe and Mn oxides, organic matter (notably high molecular weight humic and humic-Fe components), and selenium (Se); but CH_3Hg^+ and total Hg differed in their specific preferences for binding agents, implying that binding sites discriminate between CH_3Hg^+ and Hg^{2+} ions. CH_3Hg^+ was associated with sulfide and (in the spring only) with Fe oxides, whereas total Hg was associated with organic matter and Se and with DTPA- and NaOH-extractable Fe in the spring but with Mn oxide and NaOH-extractable organics in the summer. Sulfides were most abundant in May, indicating that they were eroded from bottom sediments, but Fe and Mn oxides were most abundant in the summer, probably owing to activities of filamentous iron bacteria and other micro-organisms.

Particulate Hg was 98-100% nonextractable by mild solvents such as Ca acetate, $CaCl_2$, dilute acetic acid, and (at polluted sites only) DTPA solutions, suggesting that the particulate Hg mobilized in the spring may not be readily available to organisms; association

with Se and high molecular weight humic matter also supports this hypothesis. Hg probably becomes more bio-available in the summer, as suggested by the upsurge in dissolved CH_3Hg^+ and total dissolved Hg levels, and by increases in the solubility of particulate Hg in acetic acid, DTPA, H_2O_2, and NaOH solutions, as well as an increase in the relative importance of lower molecular weight fractions of NaOH-extractable Hg (in September).

Regional variations in Hg speciation and partitioning reflected a gradient in sediment composition from wood chips near Dryden to silt-clay mud further downstream. Hg in silt-clay mud relatively far ($\geq$ 35 km) downstream from the source of pollution or in unpolluted areas appeared to be more readily solubilized by Cl^- ions or chelators such as DTPA, more readily methylated (as indicated by downstream increases in dissolved CH_3Hg^+ levels and CH_3Hg^+/total Hg ratios), and was to a greater degree organically bound (H_2O_2-extractable), and thus was probably more bio-available, than Hg in wood-chip deposits. Possible explanations include weaker binding of Hg by the mud, the more finely divided state of the mud, and improved microbial growth at lower concentrations of toxic pollutants. Owing to enrichment in sulfides and Fe oxides, resuspended wood-chip sediments were especially efficient scavengers of CH_3Hg^+.

The results indicate that any pollution abatement plan aimed at lowering the Hg levels in the biota of lakes fed by the Wabigoon River would have to include immobilization, removal, or detoxification of dissolved as well as particulate forms of Hg in the river. Possibly this could be achieved by increasing the load of uncontaminated suspended clay- and silt-sized sediments. These particulates would "scrub" dissolved Hg species from the water and subsequently deposit them in receiving basins, and would tend to bury contaminated bottom sediments, thereby suppressing the release of dissolved Hg species into the overlying water.

INTRODUCTION

The interim report of the Canada-Ontario intergovernment research group established for the investigation of mercury pollution in the Wabigoon-English-Winnipeg River system (Jackson (ed.), 1980) presented the results of geochemical studies conducted during the first year of the project (1978-1979) (Jackson and Woychuk, 1980 a & b; Parks et al., 1980). The present report gives the results of additional geochemical research carried out during the second year (1979-1980) to improve understanding of the effects of seasonally and geographically varying environmental processes on the speciation, sediment-water partitioning, and transport of Hg in the Wabigoon River. Attention was focused on the cycling of "dissolved" and "suspended" species in the river water upstream from Clay Lake, with particular emphasis on methyl mercury (CH_3Hg^+), which is regarded as the most toxic Hg species in aquatic environments. Such information is relevant to the question of the availability of Hg to fish in lakes fed by the river, and thus is needed to help establish a basis for recommending remedial action.

METHODS AND MATERIALS

Field Work

Samples of surface water were collected in the spring and summer of 1979 at the

Great Lakes Forest Products (GLFP) plant outflow, at different polluted sites along the Wabigoon River, and from two unpolluted "control" sites representing Wabigoon Lake (near the origin of the Wabigoon River) and the Eagle River (a tributary of the Wabigoon) (Fig. 1). In order of increasing distance downstream from the plant outflow, the Wabigoon River sites were at (1) the inflow and (2) outflow of Wainwright Reservoir, (3) Minnitaki, (4) Quibell, and (5) the outflow of Clay Lake. The sampling dates were April 24-28, May 9-15, July 19-24, August 2-5, and September 18-25. Operationally defined "dissolved" and "suspended" (or "particulate") phases of the water were separated in the field with an Envirodata "Sedisamp" continuous-flow centrifuge at a flow rate of 4 L/min and maximum spinning rate of 8,900 rpm. Specimens of uncentrifuged water were also taken. Water samples and centrifuge supernates were divided into acidified and unacidified subsamples for chemical analysis.

Laboratory work

All samples were stored at -40°C. until analyzed. In brief, the analytical procedures were as follows:

(a) Water samples. Total Hg was determined by flameless atomic absorption spectrophotometry (AA) with a Perkin-Elmer 403 AA unit following digestion with $KMnO_4$, H_2SO_4, and $K_2S_2O_8$ at ≈ 95°C. (Mercury Sampling & Analysis Review Committee, 1977, p. 1-11). Monomethyl mercury (CH_3Hg^+) was extracted with benzene, $NaBr/H_2SO_4$, $CuSO_4$, $Na_2S_2O_3$, and KI and estimated by means of a Tracor Micro-Tek Mt-220 gas chromatograph (GC) employing a Varian electron-capture detector (Uthe et al., 1972). Conductivity and pH were also measured. For all other analyses, water samples were passed through acid-rinsed 0.45 µm Millipore filters.

Organic carbon (org. C) was determined by Beckman 915 analyzer, and Cl^- and SO_4^{2-} by the methods of Stainton et al. (1977). After digestion with H_2SO_4/H_2O_2 under ultraviolet (UV) light (Stainton et al., 1977), total Fe, Mn, Ca, Mg, Na, and K were estimated by AA, and total N was determined by the chloramine-T method (Banoub, 1972).

(b) Sediment samples. Total Hg in suspended particulates was determined by flameless AA after digestion with $H_2SO_4/HNO_3/HCL$ and $KMnO_4/K_2S_2O_8$ at 60°C. (Mercury Sampling & Analysis Review Committee, 1977, p. 77-91). CH_3Hg^+ was extracted with toluene, $NaBr/H_2SO_4$, $CuSO_4$, $Na_2S_2O_3$, and KI and then determined by GC (Uthe et al., 1972). For determination of non-volatile sulfide (S^{2-}), samples were digested with 6 N HCl at 90°C. to convert S^{2-} to H_2S, which was precipitated with Zn acetate, solubilized with p-phenylenediamine and $FeCl_3$, and estimated colorimetrically (Strickland and Parsons, 1968; Stainton et al., 1977). The samples were analyzed for N and org. C with a Carlo-Erba CHN analyzer, and for Fe and Mn by AA after digestion with hot $HNO_3/HClO_4$ (5:1, v/v). Total Se was determined as well (Vijan and Wood, 1976). All data were calculated on the basis of oven-dry (105°C.) weight.

Operationally defined forms of Hg, Fe, and Mn were isolated by extraction with different N_2-purged solvents under an atmosphere of N_2. The extracts were wet-ashed with H_2SO_4/H_2O_2 under UV light and analyzed by AA. The following solvents and extraction sequences (indicated by arrows) were used:

(1) 1 N Ca acetate (pH 6.8) → 1 N $CaCl_2$ (pH 5.3) → 0.1 M $NH_2OH \cdot HCl$/0.1 M HNO_3 (pH 1.7) → 0.2 M NH_4 oxalate/0.1 M oxalic acid (pH 3.3) → 30% H_2O_2/1 N NH_4 acetate/6% HNO_3 (≈ 80°C., pH 2) → 0.27 M citrate/0.11 M dithionite (pH 5.3).

(2) "DTPA" (0.005 M diethylenetriaminepentaacetic acid/0.01 M $CaCl_2$/0.1 M triethanolamine) (pH 7.3).

(3) 2.5% acetic acid (pH 2.4) → 0.1 N NaOH (pH 13.0).

Ca acetate, $CaCl_2$, and acetic acid presumably extract only weakly sorbed, "exchangeable" metal fractions (Chester and Hughes, 1967; McLaren and Crawford, 1973; Rashid, 1969), and DTPA is used for extraction of "bio-available" fractions of certain metals (Follett and Lindsay, 1971). $NH_2OH \cdot HCl/HNO_3$ and oxalate solubilize "amorphous" hydrated Fe and Mn oxides, while citrate/dithionite extracts the more crystalline oxides (Chao, 1972; Gupta and Chen, 1975; McKeague and Day, 1966). NaOH extracts humic and other organic complexes (Schnitzer and Khan, 1972), and H_2O_2 liberates the total organically-bound metal fraction (Gupta and Chen, 1975). The NaOH extracts were fractionated on a column of Pharmacia Sephadex G-100 gel eluted with 0.025 M Na borate buffer (pH 9.15), and fractions (5 mL/3 min.) were analyzed for metals, org. C, and UV-visible spectral properties--notably absorbance at 465 nm (symbolized as A_{465nm}) and the absorbance ratio A_{465nm}/A_{665nm}.

Following digestion with hot H_2O_2, size frequencies of particulates were determined by sieving and by measurement of settling velocity in Na hexametaphosphate solution (M. L. Jackson, 1956), and X-ray diffraction patterns were obtained with a Philips diffractometer employing CuKα radiation. Finally, particulates resuspended in water were examined under a phase-contrast microscope.

RESULTS AND DISCUSSION

The concentrations and loadings of dissolved and particulate forms of Hg and other chemical components of the Wabigoon River were strongly dependent on environmental variables which were functions of the time of year and distance downstream from the source of pollution.

The major seasonal factors included river discharge and temperature. Discharges, and therefore bottom scour, were greatest during the spring runoff in April and May--the major influx of Wabigoon Lake water occurring in May, when a floodgate at Dryden was opened--and were minimal during July-September. Water temperatures were highest in July and August, probably causing a peak in microbial activity. The most important factors dependent on sample site included, again, the discharge, which increased in the downstream direction, and gradients in water and sediment composition resulting from downstream dilution of wood chips, dissolved solids such as Na^+Cl^-, and other pollutants discharged into the river at Dryden (Jackson and Woychuk, 1980 a & b). From the GLFP outflow to Wainwright Reservoir outflow (at Wainwright dam), the surface sediments consist principally of wood chips, but with increasing distance downstream this material grades into natural silt/clay mud. At all Wabigoon River sites the spun-down particulates consisted largely of grey silt and clay with varying proportions of wood fibre and sand-sized aggregates of silt cemented by Fe oxide, as well as occasional dark brown, sheathed, filamentous bacteria showing false branching. The micro-organisms are tentatively identified as iron bacteria (Chlamydobacteriales). In general we found that CH_3Hg^+ levels in particulate matter and water depended on environmental conditions rather than total Hg concentrations (cf. Jackson and Woychuk, 1980 a & b).

Concentrations and loadings of total and methyl mercury in dissolved and particulate fractions

At both polluted and unpolluted sites, the CH_3Hg^+ and total Hg content of particulate matter (on a wt./wt. basis) and the concentrations of particulate CH_3Hg^+ and total particulate Hg in the water (on a wt./vol. basis) were invariably highest in the spring (usually in May) and lowest in the summer (Fig. 2, A & B), although at any given sampling season the CH_3Hg^+ levels did not correlate significantly with total Hg levels. In most cases, CH_3Hg^+ was undetectable in particulate matter during the summer months. In contrast, "dissolved" CH_3Hg^+ was most abundant in the mid- or late summer (mostly during July-August) except in the Eagle River (Fig. 2C, 3). However, total "dissolved" Hg tended to peak in September at Wabigoon River sites and in May at the control sites (Fig. 2C). In both the Wabigoon and the Eagle Rivers the percentage of CH_3Hg^+ or total Hg in particulate form was highest in the spring and lowest in the summer, but both Wabigoon Lake and Clay Lake showed high percentages of particulate Hg in the summer (Fig. 2D). At all seasons "dissolved" CH_3Hg^+ levels in the Wabigoon River tended to increase in the downstream direction (Fig. 3).

The loadings of particulate CH_3Hg^+ and total particulate Hg showed a pronounced maximum in May (Fig. 4A). Total "dissolved" Hg loadings demonstrated a comparable tendency, but "dissolved" CH_3Hg^+ loadings gave a very different pattern (Fig. 4B). At Minnitaki and Quibell, "dissolved" CH_3Hg^+ loading dipped to minimal values in May and then rose progressively from May to September, whereas at the inflow and outflow of Wainwright Reservoir the values peaked during July-August. At all seasons, "dissolved" and suspended CH_3Hg^+ loadings tended to increase in the downstream direction (Fig. 5).

The seasonal patterns (Figures 2 & 4) could be explained as follows: In the spring, increased current velocity and resulting bottom scour caused resuspension and accelerated transport of sediment-bound CH_3Hg^+ and inorganic Hg, accompanied by scavenging of dissolved Hg species by the particulates and dilution of dissolved species of uncontaminated runoff; in the summer, elevated temperatures accelerated the methylation and solubilizaton of sedimentary Hg by micro-organisms, and elevated salt concentrations probably promoted solubilization of Hg from Wabigoon River sediments (see below), while the influence of dilution and sediment resuspension was relatively slight owing to reduced runoff, increased evaporation rates, and slackened flow. The high percentage of Hg in particulate form in lake waters in the summer, as contrasted with the high percentage in "solution" in river waters, suggests that "soluble" Hg is readily accumulated by the plankton of these lakes. Thus, Hg solubilized from Wabigoon River sediments in the summer and then transported into Clay Lake may be largely taken up by planktonic organisms in the lake.

The downstream increase in CH_3Hg^+ loadings (Fig. 5) can be attributed to an observed increase in the discharge of river water in the downstream direction (a widely observed phenomenon in rivers). However, the downstream increase in dissolved CH_3Hg^+ concentration (Fig. 3) appears to imply that conditions for CH_3Hg^+ production or solubilization become increasingly favorable with distance downstream from the source of pollution.

At this point, it would be appropriate to examine briefly the meaningfulness of our operational definition of "dissolved" and "suspended" fractions of Hg species. Although separation of dissolved and suspended material was limited by the imperfect efficiency of the centrifuge technique (as revealed by routine filtration of water before and after centrifugation), the usefulness and validity of the separation process and its underlying assumptions were confirmed by evidence entirely independent of the centrifuge technique: In May, the CH_3Hg^+ content of uncentrifuged water closely paralleled the particulate content of the water as determined by filtration, but during July-August the two parameters were inversely related (Fig. 6). This finding supports our conclusion that CH_3Hg^+ in the water is predominantly particulate during the spring flood but is largely in solution in the mid-summer.

Variations in dissolved and particulate components other than mercury species

Before examining in greater detail the mechanisms of Hg speciation, binding, and release, let us survey temporal and spatial variations in relevant properties of the dissolved and particulate phases of the water.

Throughout the Wabigoon River system from Wabigoon Lake to Quibell, the S^{2-} content of particulate matter peaked in May, the concentrations being highest in Wainwright Reservoir (Fig. 7A). Evidently most of the S^{2-} represents resuspended bottom sediment derived mainly from organic paper-mill detritus deposited near Dryden. In contrast, the particulate Fe and Mn fractions extracted with citrate/dithionite and H_2O_2 were most abundant during July-September (Fig. 7B), suggesting that these fractions are generated by micro-organisms -- possibly by the filamentous iron bacteria, which appeared to be most abundant in July and August at several sampling sites. The highest concentrations of dissolved Cl^- occurred in late summer and early fall (Fig. 7C), probably because dilution by runoff was relatively slight and evaporation rates were high. The organic content of suspended sediments generally declined with distance downstream from Dryden, reflecting downstream dilution of wood-chip detritus, except during July-August, when an increase from Minnitaki (at 35-36 km) to Quibell (at 70-71 km) was observed (Fig. 8A). Similarly, N levels decreased downstream in May but increased during July-August (Fig. 8 A). With the general downstream decrease in detrital organic matter, there was a corresponding increase in the abundance of clay minerals and quartz (Fig. 8B; Table 1). THe org. C and N data suggest that in the mid-summer biological activity (as represented by production of nitrogenous organic particulates) intensified with distance from the GLFP plant, possibly owing to the progressive attenuation of toxic pollutants discharged into the river. This may help to explain why dissolved CH_3Hg^+ levels increased in the downstream direction (Fig. 3).

Mechanisms of Hg speciation and sediment-water partitioning

Particulates. CH_3Hg^+ content correlates significantly with S^{2-} content for all samples of Wabigoon River particulate matter (Fig. 9A), suggesting sorption of CH_3Hg^+ by sulfides. The total Hg, however, did not correlate with S^{2-} even though Hg^{2+} ions supposedly have a stronger affinity for sulfides than CH_3Hg^+ does (Feick et al., 1972). Specific binding of CH_3Hg^+ by certain biogenic organic sulfides in the bottom sediments is a possibility worthy of future investigation.

In April and May only, particulate CH_3Hg^+ also correlated with $NH_2OH{\cdot}HCL/HNO_3$- extractable Fe (Fig. 9B) and -- to a lesser extent -- with citrate/dithionite-extractable Fe. Possibly these fractions were associated with the sulfides or represent sulfides oxidized upon being suspended in oxygenated water. The higher values of CH_3Hg^+, S^{2-}, and extractable "Fe oxide" all represent the Wainwright Reservoir sites. Evidently sulfides and Fe oxides from the highly organic, anaerobic sediments of this region are very effective scavengers for CH_3Hg^+.

The chemical affinities of total Hg differed from those of CH_3Hg^+. In April and May total particulate Hg correlated with DTPA-extractable Fe at the inflow and outflow of Wainwright Reservoir (Fig. 10A), but with total particulate org. C and Se at Minnitaki and Quibell (Fig. 10, B & C), the Se/Hg molar ratio ranging from 0.4 to 1. In July and August, however, total Hg from all Wabigoon River sites was associated with $NH_2OH{\cdot}HCl/HNO_3$-extractable Mn (Fig. 10D). Thus, in bottom sediments resuspended in the spring, Hg was probably bound to organic matter and Se, and Fe oxides or complexes, but in the summer Mn oxides--formed perhaps by microbial(?) oxidation of soluble Mn diffusing out of the sediments -- were the major Hg-binding agents.

Throughout the sampling area, 98-100% of the total particulate Hg was nonextractable by mild solvents (Ca acetate, $CaCl_2$, dilute acetic acid, and -- at polluted sites only -- DTPA solutions) (Table 2), suggesting that most of the particulate Hg resuspended by bottom scour may not be readily bio-available. The solubility of particulate Hg in acetic acid, DTPA, and NaOH solutions was greatest in the summer, possibly indicating enhanced bio-availability or biologically mediated mobilization. In the spring (and in July at Quibell alone) CH_3Hg^+ was the most abundant particulate Hg species, although the availability of this bound CH_3Hg^+ is questionable. In the summer, it would seem that an appreciable amount of the available Hg^{2+} in the sediment is converted to CH_3Hg^+, which dissolves in the water instead of being scavenged by suspended particulates (Fig. 2 & 3). After CH_3Hg^+, NaOH-extractable Hg was quantitatively most important, as might be expected from the generally strong affinity between Hg and humic matter (Jackson et al., 1980). As illustrated by Sephadex data for Minnitaki (the only Wabigoon River site for which we have such data) (Fig. 11, A-C), the NaOH-extractable Hg was preferentially bound to the higher molecular weight "humic" fractions (cf. Jackson et al., 1980), especially in the spring and mid-summer; but by September the proportion of Hg in lower molecular weight fractions had increased considerably. These results suggest the possibility that Hg complexed by humic matter is not readily bio-available but becomes more available in the late summer.

DTPA extracted only 0-2% of the particulate Hg from polluted regions, but as much as 29% and 6% from the unpolluted Wabigoon Lake and Eagle River, respectively, and comparable reults were obtained for H_2O_2-extractable Hg and CH_3Hg^+ (Table 2). We tentatively infer that Hg bound to the polluted sediments is less bio-available than Hg bound to "clean" silt/clay mud in unpolluted waters (cf. Jackson and Woycnuk, 1980 A & B). This may reflect (1) stronger fixation of Hg by binding agents in polluted sediment, (2) the existence of Hg in a more finely divided or surface-active state in clay-rich unpolluted sediments (Table 1), or possibly (3) inhibition of micro-organisms by toxic pollutants in the Wabigoon River-Clay Lake system.

Although confirmation by experiments with organisms is needed, the data for solvent-extractable Hg suggest that very little of the particulate-bound Hg -- especially in the spring, and especially in the case of highly polluted sediments -- is readily available to organisms. Conceivably, the mobilization of particulate Hg during the spring flood may have a disproportionately small impact on organisms further downstream (e.g. in Clay Lake). On the other hand, the release of soluble Hg^{2+} and CH_3Hg^+ into the water in the summer could have an important effect, which may become increasingly serious with distance downstream from the source of pollution, even though the total Hg supply in the bottom sediments falls off (cf. Jackson and Woychuk, 1980 A&B; Parks et al., 1980).

The solution phase. In the summer only (July-September), total dissolved Hg at all sampling sites of the Wabigoon River system increased with dissolved Cl^- concentration (Fig. 12). This may well represent solubilization of Hg from sediments by formation of water-soluble chloride complexes, the Cl^- levels being greatest at that time of year (Fig. 7C). The plots form two separate curves: one for the region extending from the GLFP Plant to the outflow of Wainwright Reservoir, and another one for the region extending from Minnitaki to the outflow of Clay Lake. Evidently the solubility of Hg was much lower near the source of pollution, where the surface sediments consist largely of wood chips, than further downstream, where clay and silt predominate. This supports the conclusion that Hg is more strongly bound to the wood-chip detritus than to the silt/clay mud, therefore becoming increasingly "available" with distance downstream from the GLFP plant.

In July and August -- but not at the other seasons -- "dissolved" CH_3Hg^+ correlated significantly with total "dissolved" Hg at all sites (except the GLFP outflow, where there were anomalously high Hg levels but no CH_3Hg^+) (Fig. 13). This relationship, and the fact that it occurred only in the warmest part of the year, when microbial activity was presumably greatest, suggest rapid biomethylation of solubilized Hg^{2+} diffusing out of the bottom sediments. At GLFP, microbial methylating activity may well have been inhibited by poisonous pollutants. At times of year other than mid-summer, the abundance of CH_3Hg^+ is evidently a function of environmental variables, and is independent of total Hg concentration.

Implications for pollution abatement

Any program for complete restoration of the polluted lakes and rivers-in particular, for reducing the concentrations or toxicity of Hg in the fish to background levels -- would have to include removal, immobilization, or detoxification of the Hg accumulations in river sediments *at least* as far downstream as the inflow to Clay Lake (Jackson and Woychuk, 1980a & b; Parks *et al.*, 1980), and probably throughout the Wabigoon-English-Winnipeg River system (Parks *et al.*, 1982). Otherwise, Hg released from these sediments and transported into the lakes by river water can be expected to continue contaminating the lake biota for decades, if not centuries. Our research has shown that dissolved as well as particulate forms of remobilized Hg in the river water -- notably dissolved species released from the riverbed during the summer -- would have to be taken into account in the pollution control strategy. Hg in contaminated sediments at the surface of the riverbed would have to be immobilized, removed, or detoxified. Possibly this could be achieved by increasing the load of uncontaminated suspended clay- and silt-sized sediments at selected times of year and at selected points throughout the river system. These particulates, besides "scrubbing" dissolved Hg species from the water and subsequently depositing them in receiving basins, would tend to bury contaminated bottom sediments, thereby suppressing the release of dissolved Hg species into the overlying water. Of course, this procedure could be used in conjunction with other methods such as limited dredging of selected parts of the riverbed.

Possible pollution abatement measures are discussed in greater detail in other chapters of the Final Report.

CONCLUSIONS

1. CH_3Hg^+ and inorganic Hg in Wabigoon River water are predominantly particulate during the spring flood; but in the summer, particulate forms decline sharply while dissolved forms increase. In the spring, transfer of Hg species from bottom sediments to water is due chiefly to physical erosion and resuspension of sediments by current action; but in the summer Hg is mobilized primarily by microbial activities such as methylation and by chemical processes such as leaching by dissolved chloride ions.
2. Particulate Hg species are not readily solubilized, and are probably not readily available to organisms. Thus, the particulate Hg species mobilized in the spring are probably less bio-available than the dissolved forms mobilized in the summer. Even particulate species are probably more bio-available in the summer than in the spring. Dissolved Hg transported to Clay Lake in the summer is taken up by plankton in the lake.
3. Hg bound to wood-chip deposits blanketing the riverbed near the source of pollution appears to be less readily desorbed and methylated, and therefore less bio-available, than Hg bound to the silt-clay mud which predominates further downstream and in unpolluted "control" areas.
4. In the mid-summer, dissolved CH_3Hg^+ level was a function of total dissolved Hg concentration, because the microbial transformation of desorbed inorganic Hg to CH_3Hg^+ was most efficient at that time of year. But in general, dissolved and particulate CH_3Hg^+ levels are controlled by environmental factors rather than total Hg concentration.

5. Hg species in particulates are associated with sulfides, iron and manganese oxides, organics (notably high molecular weight humic components), and selenium; but their preferences for particular binding agents vary with season, local environment, and type of Hg species. CH_3Hg^+ and inorganic Hg differ in their specific affinities for binding sites, indicating differential distribution within the particulate matter.

6. Any program for pollution control, short of total removal of Hg from bottom sediments, would have to include immobilization, removal, or detoxification of the dissolved as well as the suspended forms of CH_3Hg^+ and inorganic Hg in Wabigoon River water upstream from the lakes through which the contaminated water flows.

ACKNOWLEDGMENTS

THe research was funded jointly and equally by the governments of Canada and Ontario in accordance with the Canada Water Act. X-ray diffraction analyses and certain chemical analyses of water samples were done by technicians in the Federal Department of Fisheries and Oceans at the Freshwater Institute. We thank Dr. William Warwick for the use of his microscope.

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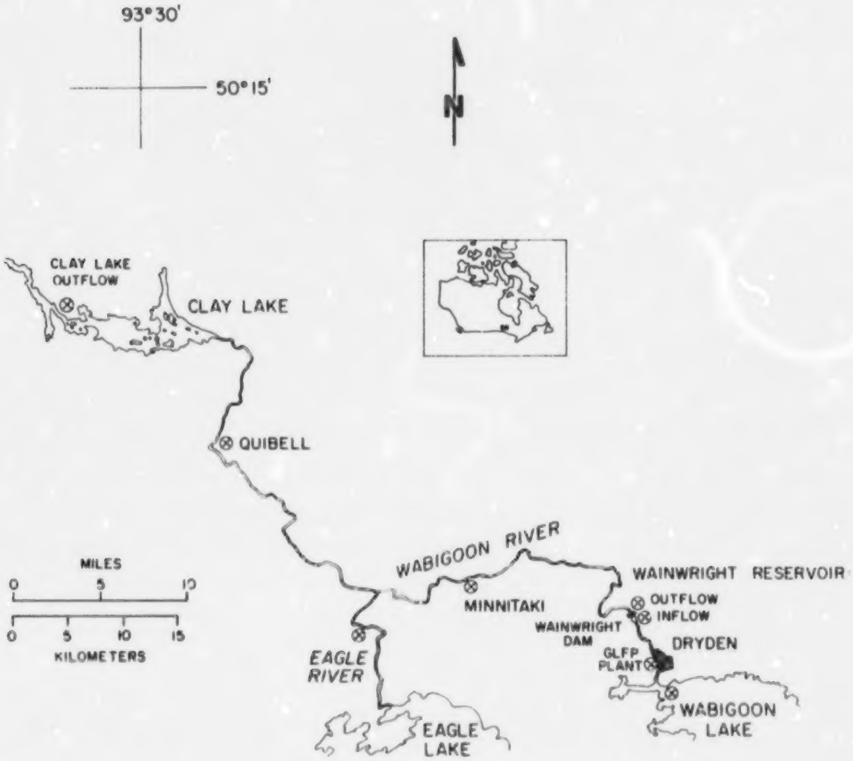
Table 1. Relative abundance of clay (< 2μm inorganic fraction as determined by settling velocity) and organic matter (determined by weight loss after H_2O_2 digestion) in suspended particulates collected in July and August.

Sample site	Date of collection	% clay	% organic matter
Wabigoon Lake	July 19	94.0	2.05
GLFP outflow	Aug. 3	33.3	60.9
Wainwright Reservoir outflow	July 24	39.4	4.80
Quibell	July 23	71.4	13.9

Table 2. Percentages of total particulate Hg in the form of CH_3Hg^+ and various solvent-extractable fractions at polluted Wabigoon River sites and unpolluted control sites at different times of year. "n. d." means no data.

Fraction	Season	Percentage of total Hg Unpolluted sites	Polluted sites
$CaCl_2$	April	n.d.	0*
	May	n.d.	0 - 0.133
	July-Aug.	0	0 - 0.104
	Sept.	0	0 - 0.0135
Acetic acid	April	0	0
	May	0 - 0.451	0 - 0.0649
	July-Aug.	0.426 - 0.845	0.219 - 1.86
	Sept.	0*	0
DTPA	April	n.d.	n.d.
	May	0*	0*
	July-Aug.	5.97 - 29.4	0 - 0.0494
	Sept.	2.35	2.02
CH_3Hg^+	April	52.5 - 60.4	6.86 - 29.0
	May	100	1.13 - 12.0
	July-Aug.	0	0 - 13.6
	Sept.	0	0
NaOH	April	1.58 - 2.65	0.0861 - 3.47
	May	0.794 - 7.10	0.0927 - 1.52
	July-Aug.	1.01 - 59.0	2.01 - 4.77
	Sept.	2.83*	0.0784 - 24.5
H_2O_2	April	n.d.	0.00390 - 0.0140
	May	n.d.	0.00654 - 0.0329
	July-Aug.	2.32 - 4.00	0.0878 - 0.501
	Sept.	0 - 1.45	0.0840 - 0.743

*Only one sample represented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MINNITAKI
WAINWRIGHT RESERVOIR
OUTFLOW
INFLOW
WAINWRIGHT DAM
DRYDEN
GLFP PLANT
EAGLE RIVER
EAGLE LAKE
WABIGOON LAKE

Fig. 1. Map of the field area showing sampling sites ⊗ and location of the region within Canada (inset).

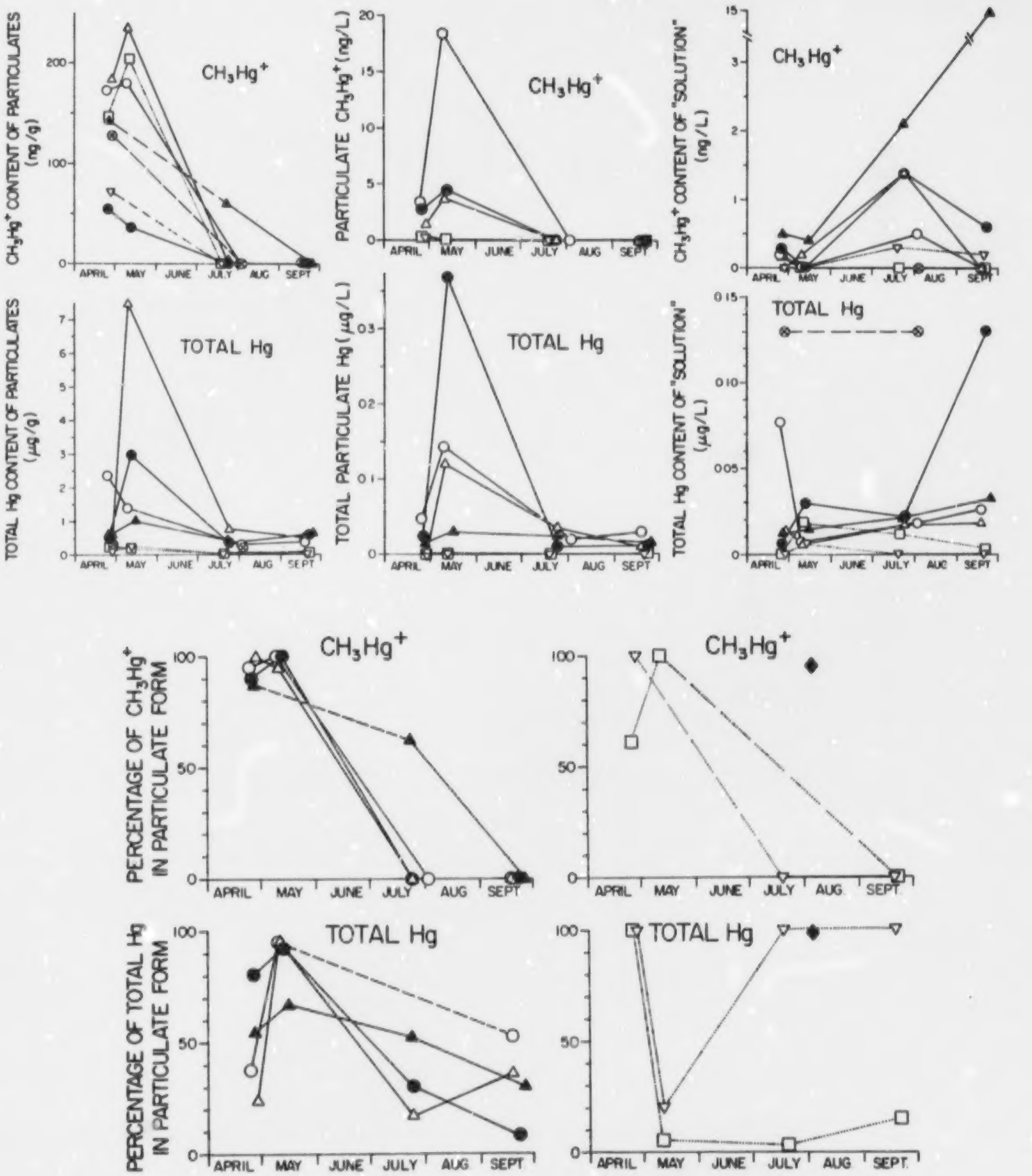

Fig. 2. Seasonal variations of (A) CH_3Hg^+ and total Hg content of spundown particulates, (B) particulate CH_3Hg^+ and total Hg concentration per unit volume of water, (C) CH_3Hg^+ and total Hg content of centrifuge supernate ("dissolved" phase), and (D) percentages of the CH_3Hg^+ and total Hg in particulate form at polluted and "control" sites.

Explanation of symbols: see Fig. 4.

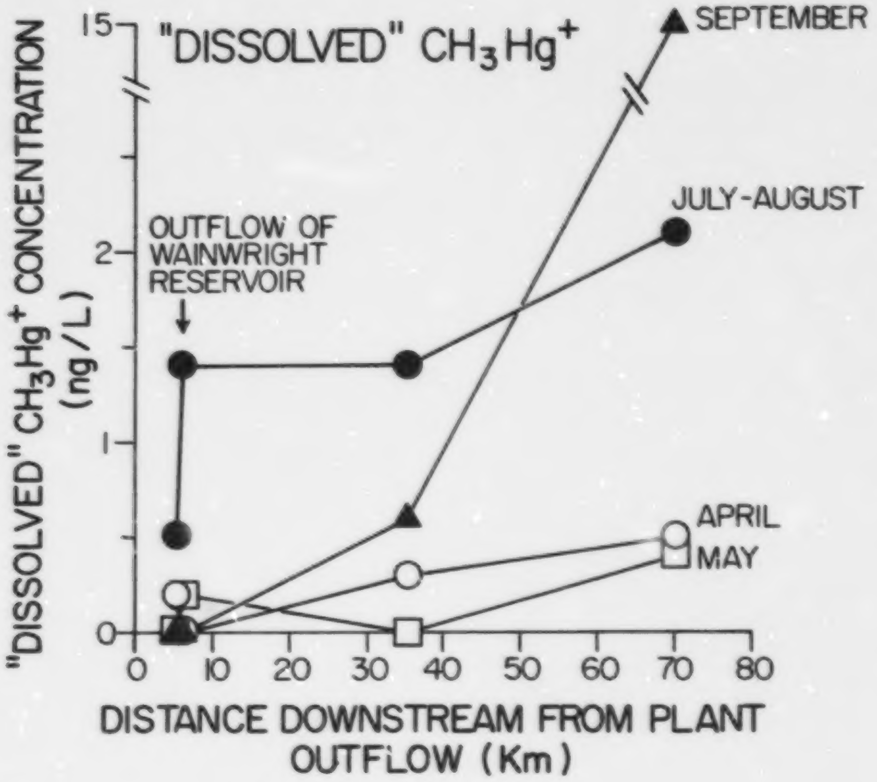

Fig. 3. "Dissolved" CH_3Hg^+ content of Wabigoon River water at different seasons as a function of distance downstream from GLFP outflow.

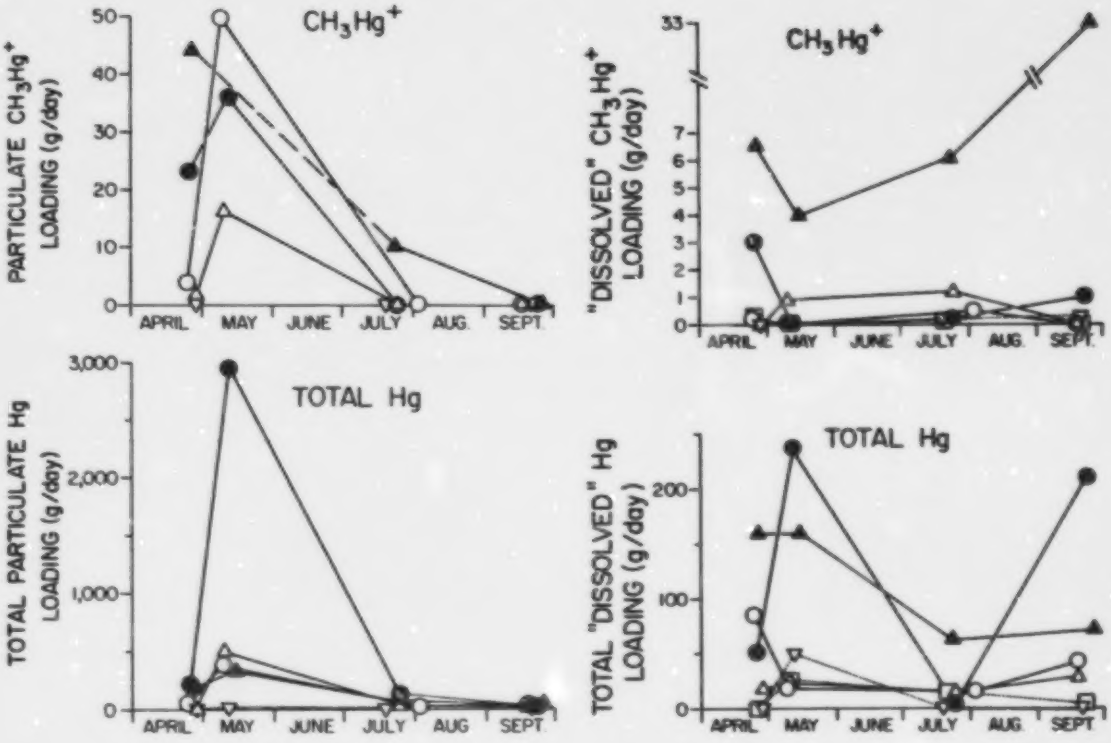

Fig. 4. Seasonal variations of (A) particulate and (B) "dissolved" CH_3Hg^+ and total Hg loadings at polluted and "control" sites.

Explanation of symbols:

Polluted sites (———): GLFP outflow ⊗, Wainwright Reservoir inflow ○, Wainwright Reservoir outflow △, Minnitaki ●, Quibell ▲, Clay Lake outflow ◆.

Control sites (......): Wabitoon Lake ▽, Eagle River □.

Broken lines signify missing data.

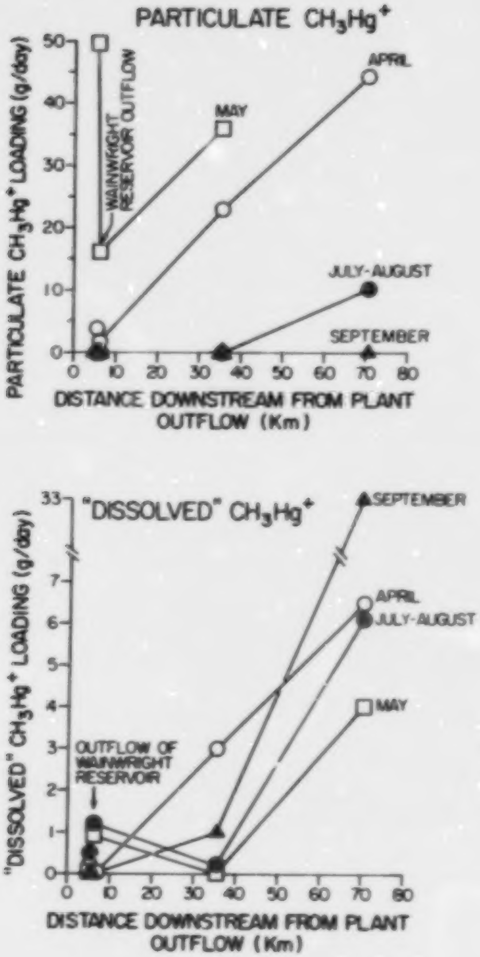

Fig. 5. Particulate (A) and "dissolved" (B) CH_3Hg^+ loadings in the Wabigoon River at different seasons as functions of distance downstream from GLFP outflow.

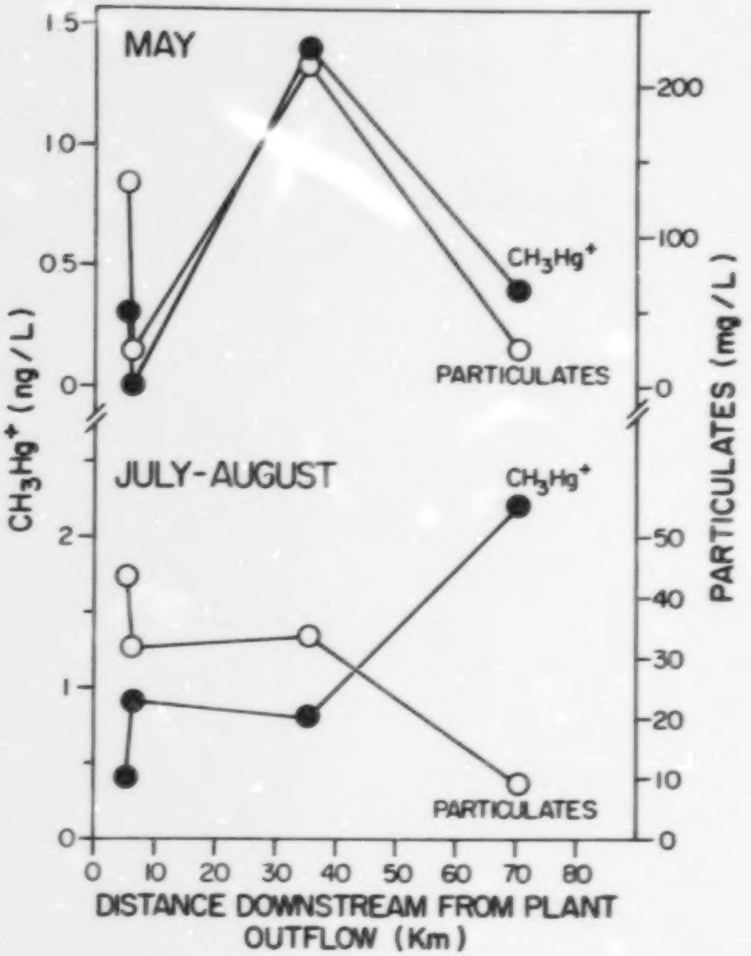

Fig. 6. Concentrations of CH_3Hg^+ (●) in uncentrifuged water, and total particulates (○) as determined by filtration (using 2 µm filters) at sampling sites along the Wabigoon River in May and July-August.

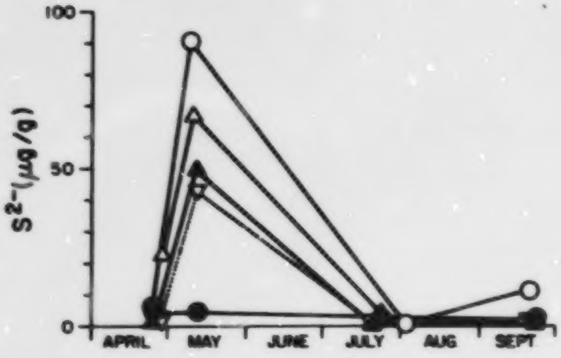

Fig 7A

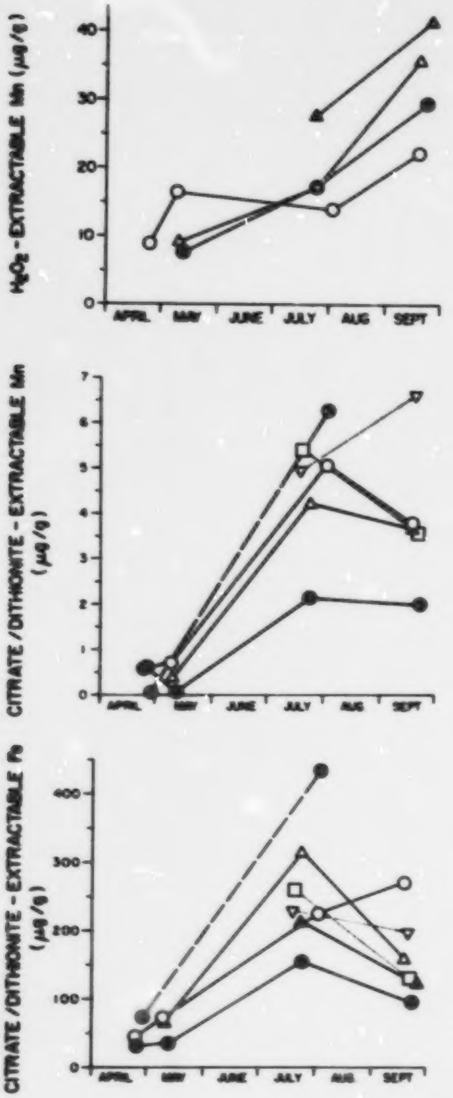

Fig 7B

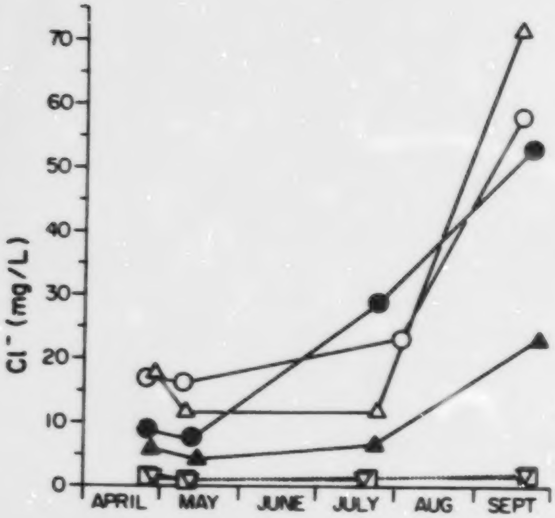

Fig 7C

Fig. 7. Seasonal variations of the concentrations of (A) non-volatile sulfide, (B) H_2O_2-extractable Mn and citrate-dithionite-extractable Fe and Mn in particulates, and (C) chloride in solution, at polluted and control sites. Explanation of symbols: See Fig. 4.

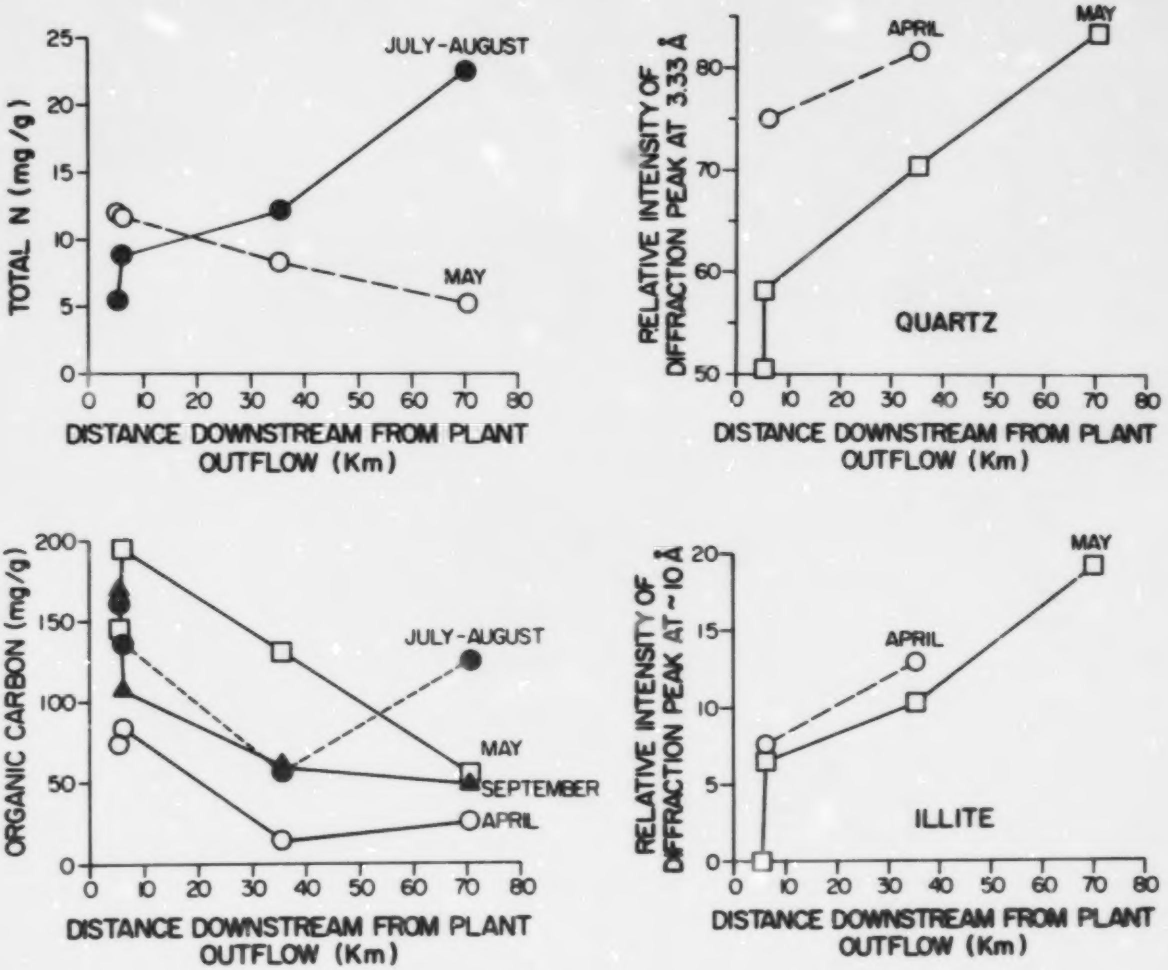

Fig. 8. Concentrations of (A) organic carbon and nitrogen and (B) illite and quartz in Wabigoon River particulates at different seasons as functions of distance downstream from GLFP outflow.

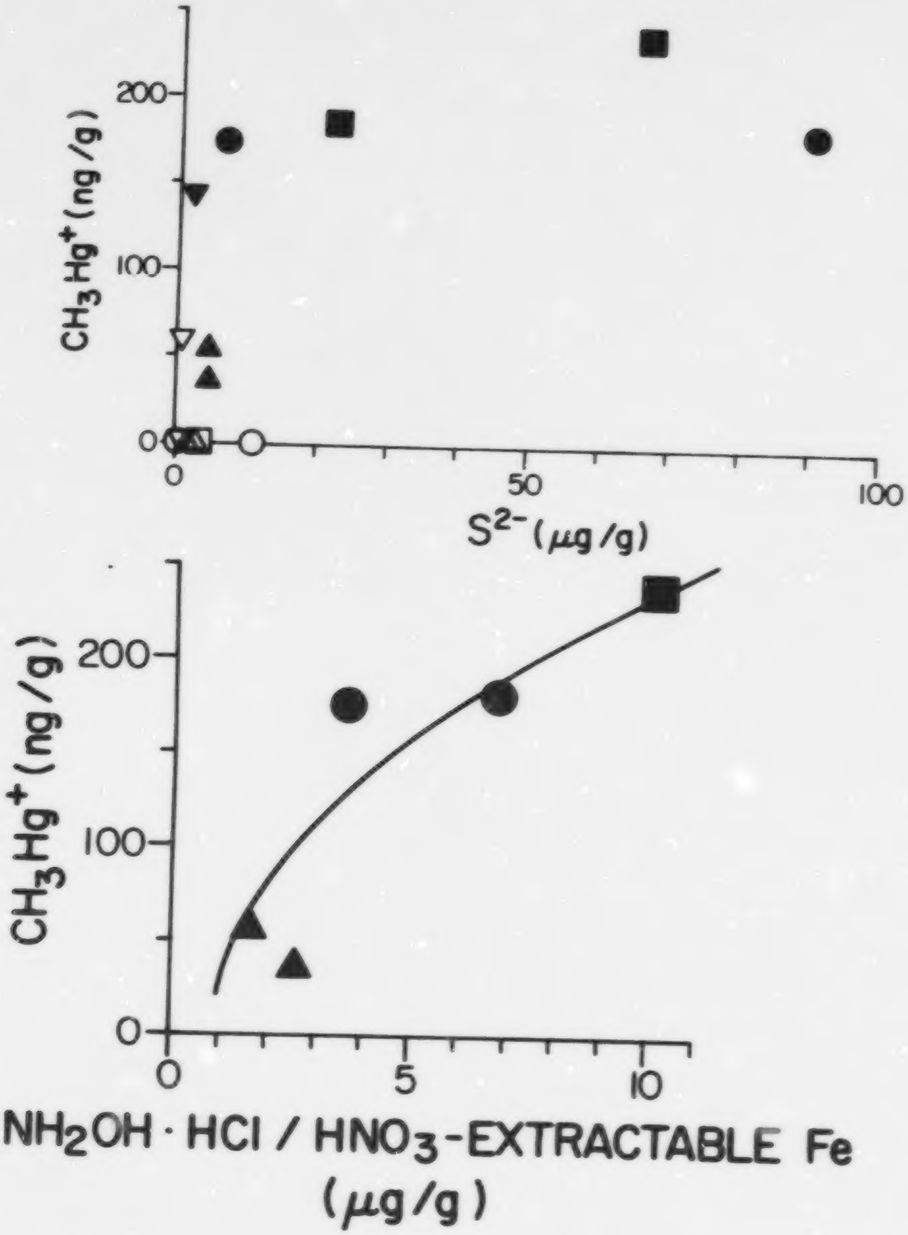

Fig. 9. Relationships between CH_3Hg^+ concentration and the concentrations of (A) sulfide ($r = 0.740$; $P > 0.001, < 0.01$) and (B) $NH_2OH \cdot HCl/HNO_3$ – extractable Fe ($r = 0.929$; $P > 0.02, < 0.05$) in Wabigoon River particulates during April-May (black symbols) and July-September (white symbols)..

Relationship of symbols to sample site:

Wainwright Reservoir inflow ●, ○; Wainwright Reservoir outflow ■, □; Minnitaki ▲, △; Quibell ▼, ▽.

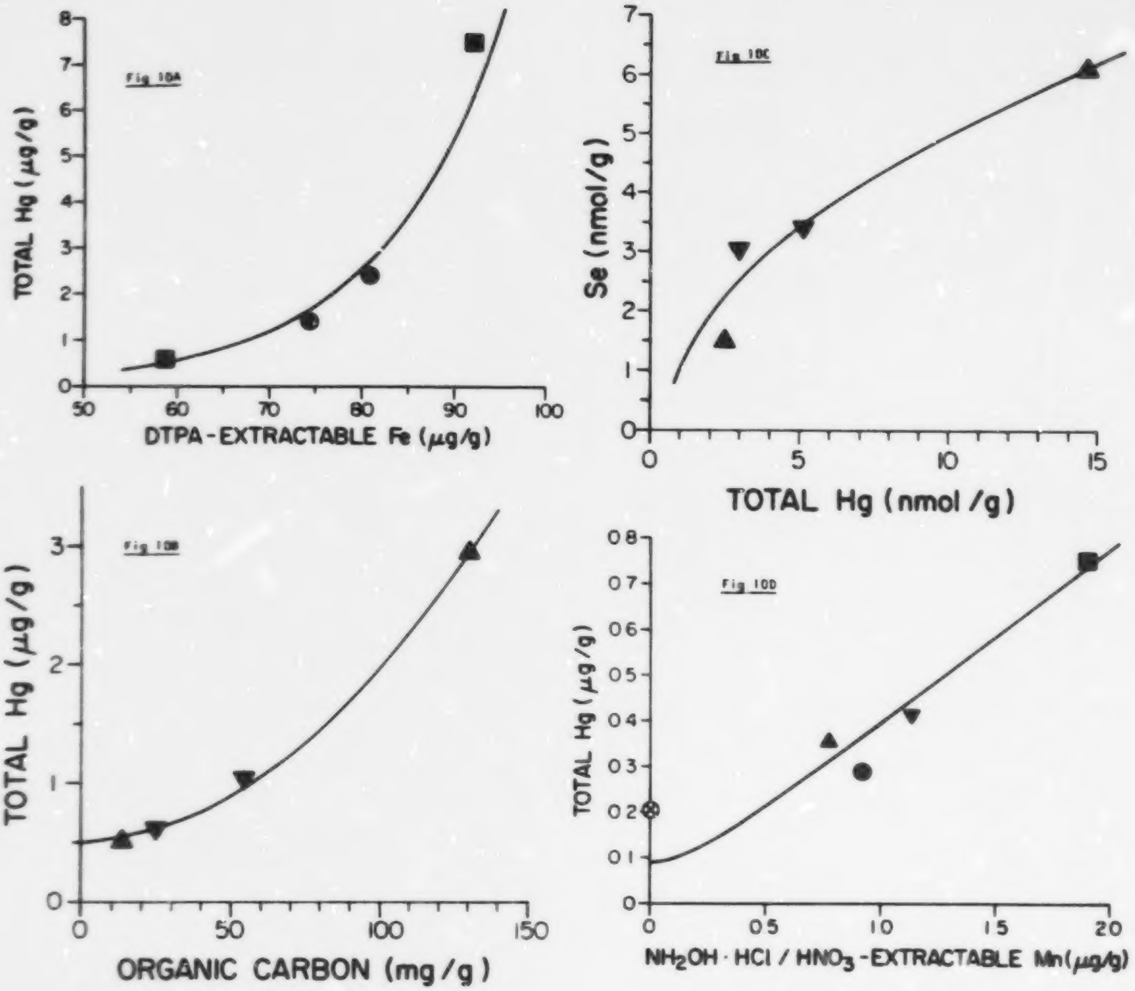

Fig. 10. Relationships between total Hg and other constituents in Wabigoon River particulates during April-May (A-C): Hg concentration plotted against the concentrations of (A) DTPA-extractable Fe at Wainwright Reservoir inflow (●) and outflow (■) (r = 0.986; P > 0.01, < 0.02), and (B) organic carbon at Minnitaki (▲) and Quibell (▼) (r = 0.999; P > 0.001, < 0.01); (C) selenium content plotted against Hg content at Minnitaki (▲) and Quibell (▼) (r = 0.989; P > 0.01, < 0.02).

D. Relationship between total Hg and $NH_2OH \cdot HCl/HNO_3$-extractable Mn in Wabigoon River particulates during July-August (GLFP ouflow ⊗ ; symbols for other sites are the same as in Fig. 10, A-C) (r = 0.985; P > 0.001, < 0.01).

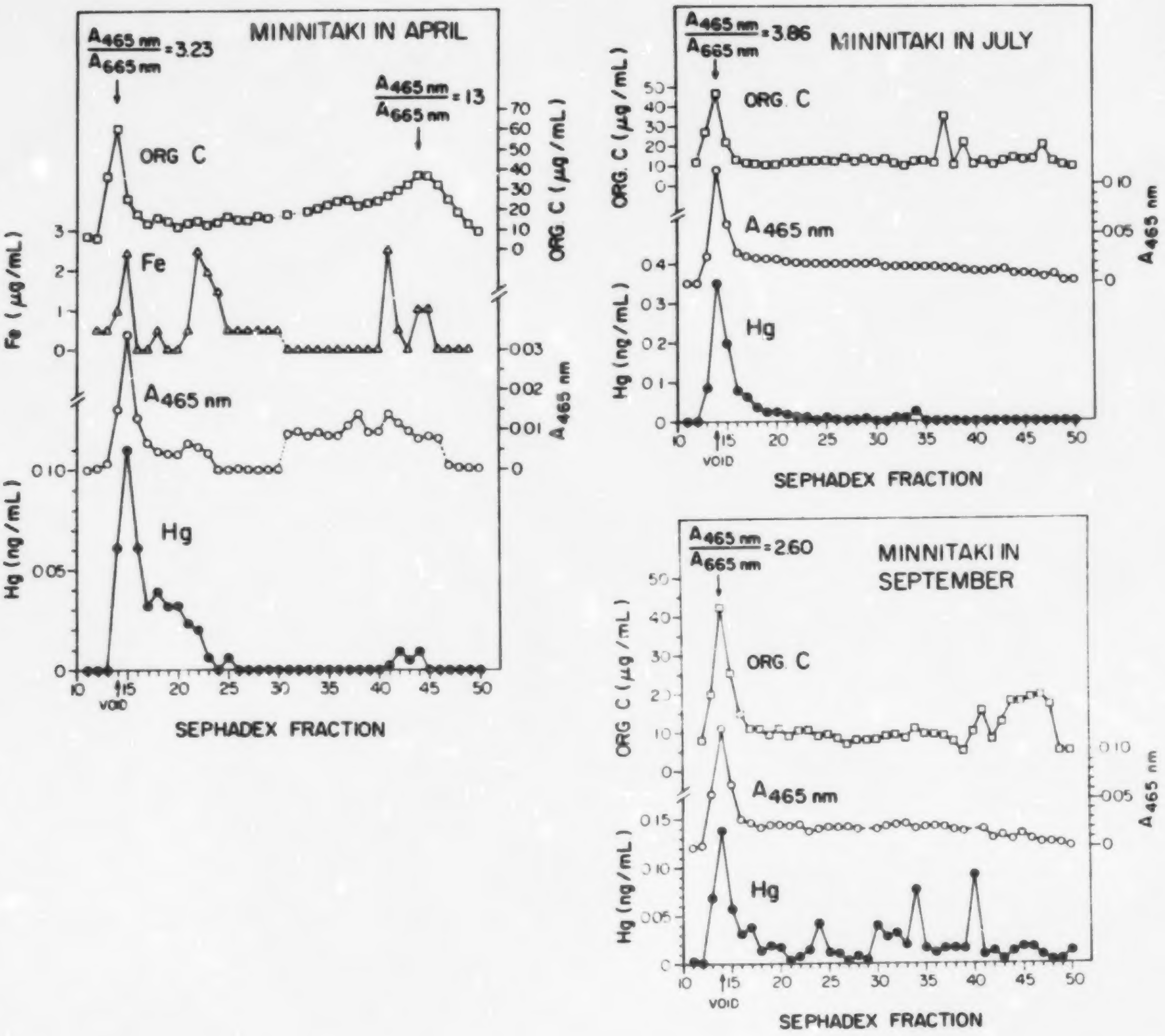

Fig. 11. Sephadex data for NaOH extracts of Minnitaki particulates in April, July, and September. In theory, molecular size is greatest in the "void" fraction and decreases with increasing fraction number.

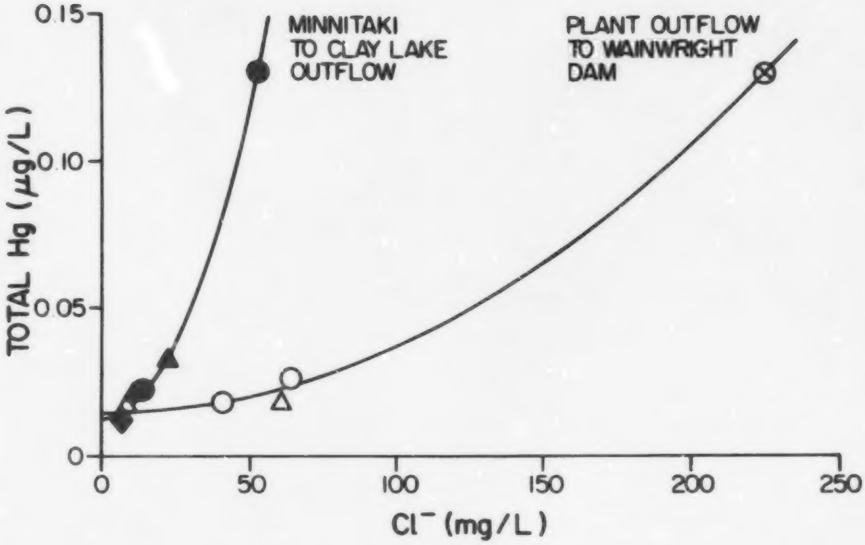

Fig. 12. Relationship between total Hg and chloride in solution phase of water in the Wabigoon River system from GLFP outflow to Wainwright dam ($r = 0.998$; $P < 0.001$) and from Minnitaki to Clay Lake outflow ($r = 0.999$; $P < 0.001$) during July-September.

Explanation of symbols: See Fig 4.

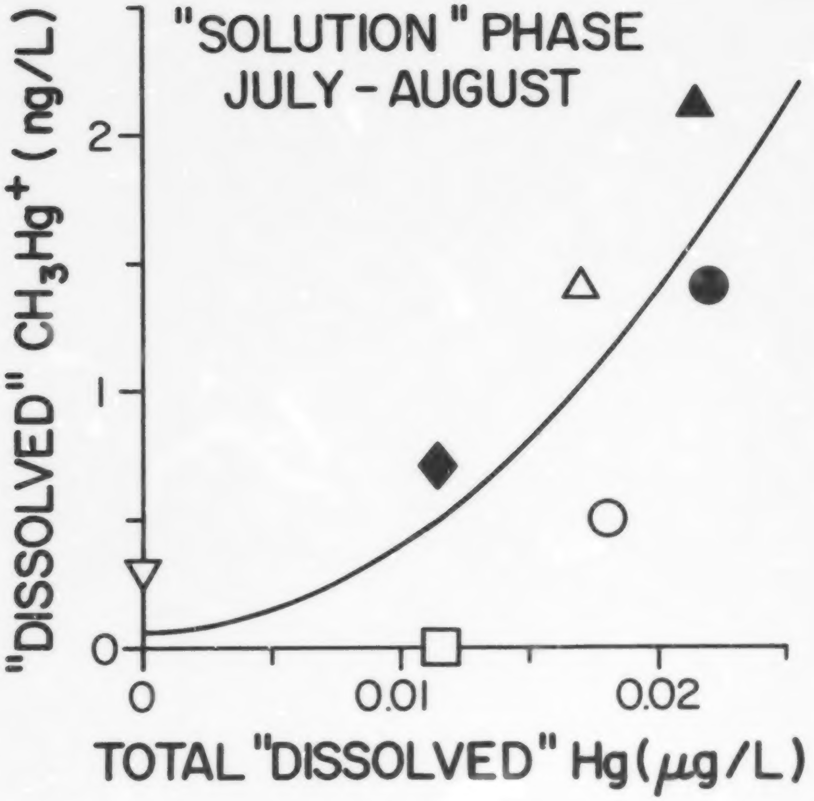

Fig. 13. Relationship between "dissolved" CH_3Hg^+ and total "dissolved" Hg at polluted and unpolluted sites during July-August ($r = 0.794$; $P > 0.02, < 0.05$). Explanation of symbols: see Fig. 4.

MERCURY POLLUTION IN THE WABIGOON-ENGLISH-WINNIPEG RIVER SYSTEM: CONCLUSIONS AND RECOMMENDATIONS BASED ON RESULTS OF THE TWO-YEAR JOINT STUDY BY THE GOVERNMENTS OF CANADA AND ONTARIO

by

Togwell A. Jackson

"We were contented to let things remain as the Great Spirit made them. They [the white men] were not, and would change the rivers if they did not suit them."

Hin-mah-too-yah-lat-kekht (Chief Joseph),
Nez Percé tribe

"Progress to me just means pollution. And killing. Killing our fish, our way of life. Maybe killing our children."

Josephine Mandamin
(White Dog band, Ojibway tribe)

CONCLUSIONS

The research team appointed by the governments of Canada and Ontario undertook its two-year study of mercury pollution in the Wabigoon-English-Winnipeg River system with the intention of establishing a scientific basis for recommending remedial action. From the standpoint of relevance to this objective, the principal conclusions of the investigation could be summarized as follows:

- The present mercury problem is due principally to the approximately 10 metric tons of mercury discharged into the Wabigoon River between 1962 and 1970, together with a smaller amount discharged between 1970 and 1975. After 1975, small detectable amounts of mercury have continued to leak from the paper plant into the river.

- Most of the mercury is bound to bottom sediments of the rivers and their associated lakes. Methylation of mercury is occurring in surface sediments and flocculated colloids, and probably in the water column. Methyl mercury and other forms of mercury in these surficial deposits continually contaminate the overlying water and its biota by going into solution (especially in the summer) or by resuspension of particulate matter to which they are sorbed (especially during the spring flood and other episodes of strong current action). Fluvial transport of mercury species remobilized from sediments causes contamination further downstream. Thus, the surface waters and biota - notably pelagic fish - of lakes in the river system are repeatedly contaminated with methyl mercury introduced by inflowing river water. Methyl mercury is also generated in the lakes themselves, and fall overturn brings hypolimnion accumulations of methyl mercury to the surface, whence they are flushed downstream. Mercury is probably more bio-available in the summer, when it is most readily dissolved and methylated, than during the spring flood, when it is mainly bound to sedimentary particles and is relatively insoluble. Clay Lake tends to trap mercury introduced by the river - presumably owing to deposition of particulate mercury - but is not a net sink for methyl mercury.

- About half of the mercury originally discharged at Dryden has been transported beyond Clay Lake, and only about a fourth of it remains in the riverbed above Clay Lake. Mercury contamination of bottom sediments, water, and fish in the Wabigoon-English-Winnipeg River system extends at least as far as the Manitoba border. Fish throughout the river system are unfit for unlimited human consumption owing to mercury contamination. Downstream from the source of pollution, mercury concentrations in sediment, water, and pelagic fish tend to decrease but virtually level off below Ball Lake; sedimentary mercury drops more dramatically with distance than mercury in water and biota.

- From Dryden to Ball Lake, methyl mercury levels in bottom sediments show no significant variation with distance from the source of pollution, even though total mercury levels decline progressively by an order of magnitude. Methyl mercury levels in the sediments, suspended particulates, and water are related to environmental factors, including temperature, nutrient supply, microbial activity, primary production, dissolved oxygen, pH, and the nature and abundance of mercury-binding substances such as sulfide, oxides, clay minerals, and organic matter; but, except under special circumstances, methyl mercury does not correlate significantly with total mercury. Methyl mercury production is stimulated by anaerobic microbial activity, which is favored by warm summer temperatures, degradable organic matter and other nutrients, and low dissolved oxygen levels. With increasing distance downstream from Dryden, sedimentary mercury, while decreasing in abundance, becomes increasingly available and more readily methylated. This trend in mercury speciation may be related to a comparable downstream gradational change in sediment composition from decomposing wood chips (mainly concentrated behind Wainwright dam) to clay-silt mud, and a corresponding increase in the proportion of weakly sorbed (potentially bio-available?) forms of mercury, and may also reflect a downstream increase in the intensity of microbial activity (owing to attenuation of toxic pollutants with distance from Dryden?). The solubility of mercury in Wabigoon River sediments is enhanced in the summer, owing at least in part to elevated levels of dissolved chloride. Evidence for moderate depression of methylating activity was found in Clay Lake sediments and in the river near the paper plant, but nowhere in the Wabigoon River system do environmental conditions preclude the formation and sediment-water partitioning of methyl mercury - not even in the relatively sulfide-rich west basin of Clay Lake.

- Suspended clay-sized, predominantly inorganic sediment blocks the uptake of mercury by the biota. Organic sediment composed largely of humic matter was found to be less effective.

- Mercury-contaminated bottom sediment is being buried by less contaminated sediments laid down on top of it.

- Cleansing of the contaminated river system (e.g. by burial of contaminated sediment) with concomitant lowering of the mercury levels in the fish is a slow process (especially since methylation rates may be high even where total mercury levels are relatively low). Restoration of the system by natural processes alone would probably take many decades.

- Selenium introduced into aquatic environments as a selenite salt obstructs uptake of mercury by fish and may reduce the toxicity of mercury under some circumstances according to reports in the literature.

RECOMMENDATIONS FOR REMEDIAL ACTION

- Present mercury discharges from the paper plant must be further reduced as soon as possible by upgrading of the plant's facilities for treatment and disposal of wastes. According to information received from the Ontario Ministry of the Environment, the Great Lakes Forest Products Company is, in fact, renovating the plant for the purpose of attaining this goal. The renovations involve installation of a primary clarifier together with lagoons for secondary treatment; in addition, old sewer pipes are to be replaced.

- A program for restoration of the river system should be undertaken if the mercury levels in fish are to be lowered to the range that is considered acceptable for unlimited human consumption ($\leq$ 0.5 ppm) in a reasonable length of time. Natural processes alone would take an excessively long time (long, that is, compared with the lifetimes of the people whose health and economic well-being have been adversely affected by the mercury pollution). If successful, the program of remedial action would be of benefit to all people who have a vital interest in the edible fish populations of the river system, and would help to redress the harm done to inhabitants of Northwestern Ontario (notably Ojibway Indians of the White Dog and Grassy Narrows bands) who have depended on these resources for food and income; it would also help to prevent further mercury contamination in the south basin of Lake Winnipeg.

- Although much of the mercury taken up by the aquatic biota comes from the ambient water, most of this recycled mercury emanates from the bottom deposits. Therefore, a reasonable approach would be to remove or immobilize the sedimentary mercury accumulations. Since the mercury pollution extends far beyond Clay Lake, and since mercury shows a tendency to become more available and more readily methylated with distance downstream from the source of pollution (at least, as far as Ball Lake) even though the total mercury concentration decreases, remedial treatments which are limited to the region between Dryden and the outflow of Clay Lake (for instance, dredging or the installation of ponds for accumulation and chemical treatment) would probably not be sufficient to solve the problem. The entire Wabigoon-English-Winnipeg River system should be affected by the treatment. Dredging this vast region is obviously out of the question, as the expense and technical difficulties would be prohibitive. On the other hand, selective dredging largely limited to the thick accumulations of mercury-contaminated wood chips near Dryden, combined with immobilization of the remaining mercury by burial under uncontaminated clay and silt derived from the river system itself and redistributed by current action, does seem to be a feasible possibility. Specifically, the method is envisioned as follows:

(1) First, the thick mass of mercury-contaminated wood fragments which have accumulated on the riverbed between Dryden and Wainwright dam should be completely removed. Owing to their continual disruption by gas bubbles and their loose packing, these deposits could never be adequately covered by clay and silt, and if left alone they would continue to pollute waters further downstream with methyl and inorganic mercury for an indefinitely long time. Conventional dredging techniques could be used, but a possible alternative would be to employ a supposedly more economical recently designed invention for in situ removal of mercury from sediments (CBCL Ltd., 1981) or environmental engineering techniques pioneered in Sweden (J. Fitchko, International Environmental Consultants Ltd., Toronto (personal communication)). After removal of mercury-contaminated wood fragments behind Wainright dam, hydraulic excavation of the entire riverbed between Dryden and Clay Lake could be attempted in order to flush away as much as possible of the remaining surficial organic deposits (scum and wood chips), which might interfere with burial. In any case, regardless of what techniques are used for physical removal of Hg from the riverbed, the possibility that disturbance and resuspension of contaminated sediment might temporarily aggravate the Hg problem by accelerating the biomethylation and bio-accumulation of Hg would have to be examined.

(2) Following this preliminary "cleansing" of the riverbed near Dryden, uncontaminated clay, silt, and fine sand would be pumped out of Wabigoon Lake and the Eagle Lake-Eagle River system, and would be resuspended in the Wabigoon River. The river would then automatically transport, sort, and deposit this sediment, eventually burying the mercury-contaminated material (assuming that erosion of the riverbed did not exceed deposition). Possibly dissolved iron or manganese salts could be mixed with the slurry to form an oxide coating on the clay, thereby promoting uptake of mercury. Inasmuch as Wainwright dam would impede the downstream transport of Wabigoon Lake sediment, it might be necessary either to demolish the dam or to install machinery for keeping the sediment in suspension, thus preventing most of it from settling out behind the dam. Inasmuch as Clay Lake and the other lakes of the river system would trap much of the suspended sediment load introduced by the rivers, thereby preventing it from moving further downstream, it would probably be advisable to resuspend river sediments periodically just downstream from each of the major lakes of the system, or else to pump sediments out of the lakes themselves and into their outflows. In any case, the task of distributing and depositing the clean sediment throughout the system would be left to the river itself. The role of the "environmental engineers" would be to remove the bulk of the wood chips and to bring large quantities of sand, silt, and clay into suspension from time to time over a period of years. Probably the most auspicious time for resuspension and long-distance transport of uncontaminated sediment would be during the spring floods, when current velocities are greatest. Upon burial of the mercury accumulations under a few centimeters of clean sediment, microbial activity would be stifled, and the release of mercury species into the water column would

effectively cease (barring renewed exposure of the mercury owing to subsequent erosion). Of course, the success of this approach would depend in part on whether the river valley is undergoing net aggradation or erosion. If there is a long-term tendency toward aggradation, the older, contaminated sediments will tend to be covered by more recent uncontaminated sediments, as has indeed been observed in a number of cores from lakes in the river system and from Wainwright Reservoir; but progressive lowering of the base level (for instance, because of gradual uplift of the land surface) would cause net erosion of the riverbed, possibly leading to exposure of buried mercury-rich horizons and renewed pollution. Therefore, a geological and hydrological survey of the river system, with further examination of cores from the river channel (as opposed to lake basins in the river system) and estimation of rates of sedimentation and erosion may be required before any firm commitment is made to the concept of burying the contaminated sediments.

(3) If possible, the contaminated fish - especially the larger, older ones - should be systematically removed en masse from the river system, which could then be restocked with uncontaminated fish from hatcheries. Local inhabitants - notably members of the Grassy Narrows and White Dog bands of the Ojibway nation - could be employed to perform this task.

- Further research, including whole-lake experiments, is warranted to ascertain the potential usefulness of large-scale selenium application as a method for rendering the mercury nontoxic. Following wholesale excavation of wood-chip sediments between Dryden and Wainwright dam, the introduction of selenium as a selenite salt might be considered as a possible alternative to the burial of contaminated river and lake sediments with clean mud. However, this method must not be employed unless exhaustive study has ruled out any possible hazard arising from the selenium itself. Problems that could, theoretically, arise from the large-scale introduction of selenium include selenium poisoning, disruption of nutrient trace element cycles, and alteration of the species composition or biochemical functions of the microbial populations, with unforeseen effects (Jackson, T.A., unpublished experimental data). As with other manipulations of natural environments, unforeseen deleterious consequences could occur. On the other hand, the selenium method does offer a possible advantage over burial: presumably it would be independent of fluctuations in the cycle of erosion and deposition, whereas the success of the burial method would depend on the mercury remaining permanently buried - perhaps a rather unrealistic expectation considering the usual vicissitudes of Earth history. The selenium, having once united with the mercury, would probably remain with it despite variations in external conditions. Burial and selenium treatment, of course, are not mutually exclusive: the two methods could conceivably be combined - for instance, by mixing selenite solution with the slurry formed on resuspension of uncontaminated sediment.

REFERENCES

CBCL Ltd., 1981, Mercury reduction in sediments: Report prepared by CBCL Ltd. (Halifax, Nova Scotia) and associates under contract for the Department of the Environment (Government of Canada). Contract serial no. of Dept. of Supply and Services, Government of Canada: 1SS80-00022.

C. FACTORS CONTROLLING MERCURY BIOACCUMULATION IN AQUATIC ECOSYSTEMS

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ACKNOWLEDGEMENTS

The research was funded jointly and equally by the governments of Canada and Ontario in accordance with the Canada Water Act and with the guidance of the Steering Committee.

The X-ray diffraction analyses of suspended sediments, and certain chemical analyses of water samples, were done by the technical staff of the Chemistry Research and Analytical Services section, Freshwater Institute (Federal Department of Fisheries and Oceans), whose assistance is gratefully acknowledged. We also thank Dr. William Warwick for the use of his microscope.

Useful discussions were held with other members of the federal-provincial research team and with Dr. A.L. Hamilton, whose interest and helpful comments on the results of the study are much appreciated.

1. A SYNTHESIS OF RECENT RESEARCH ON THE ENGLISH-WABIGOON RIVER SYSTEM WITH A VIEW TOWARDS MERCURY AMELIORATION

J. W. M. Rudd, M. A. Turner, A. Furutani, B. E. Townsend, A. L. Swick

I. INTRODUCTION

The following is a synthesis of information on mercury pollution obtained by Federal (DFO and DOE) and Ontario Government research teams working on the English-Wabigoon River system since 1977. The overall objective of the three research teams was to understand mercury cycling in the system to a point where specific amelioration procedures could be recommended with reasonable confidence. The Ontario and DOE teams investigated the mercury problem by studying the English-Wabigoon system in its present state. They sampled sediment, water, and biota at various sites on the system from Wabigoon Lake to the Manitoba-Ontario border. This was intended to provide a better understanding of the quantities and forms of mercury moving down the system, sediment water - biota interactions, and seasonality of mercury movement. Clay Lake was sampled co-operatively by Ontario and DFO teams. However much of the DFO effort was expended on large ecosystem level enclosure experiments and on direct assays of mercury methylation by natural microbial communities of the river system. These experiments were designed to provide a better understanding of the mechanisms of movement of mercury into biota and to try and identify key factors controlling the rate of mercury bioaccumulation by fish. In addition the DFO team also tested certain proposed amelioration ideas.

The comparative and experimental approaches of the research teams have resulted in information that is mutually supportive. When these results are viewed together they provide a much better understanding of mercury cycling in the system and point the way towards practicable amelioration procedures.

II. METHODS

The Ontario and DOE teams sampled the English-Wabigoon system at specific sites from Wabigoon Lake to the Manitoba-Ontario border. Samples for total mercury concentrations in sediments, water and biota and methyl mercury in water were taken on a fixed schedule. They were analyzed at the Freshwater Institute and by OME using atomic absorption spectrometry and by gas chromatography (Parks et al. 1982; Jackson et al. 1982). Data were interpreted by a mass balance approach and by a comparative approach in which partitioning of mercury between compartments within the system was examined.

The DFO team concentrated on experiments carried out in 10^5 L plastic enclosures located in Clay Lake. These enclosures contained complete ecosystems, including small fish (dace, juvenile white sucker, and young of the year perch), which grew on food produced in the enclosures during the experiments. Movement of mercury and selenium through these ecosystems was followed radiochemically. Each experiment consisted of two control enclosures plus test enclosures in which the ecosystem in the test enclosure was perturbed in a controlled manner by the addition of nutrients (Section 5), bottom sediments (Section 2), selenium (Sections 3,4), or by the presence of a plastic bottom which isolated the water column from the sediments (Rudd et al. 1980a,b). The results of these experiments were interpreted by comparing the rates of movement of the isotopes through the ecosystems and into biota between the control and test enclosures.

In addition the DFO team also developed a radiochemical method which is capable of measuring mercury methylating activity by natural communities within a short incubation period (Section 6). Using this method it was discovered that mercury is methylated in the water column (Section 6) and in the intestines of fish (Section 7). These methylation sites are in addition to the previously known methylation activity in sediments. This radiochemical method has since also been used at the Experimental Lakes Area and some of these data are included in this discussion.

To provide further insight into our Clay Lake results and assist in the understanding of mercury cycling in the English-Wabigoon system we have also included recent unpublished research carried out on the Churchill-Nelson River system by another Freshwater Institute team headed by R. Hecky (in prep). This system is similar to the English-Wabigoon system in that it is a river-lake system which is also dominated by the deposits of glacial clay. It has recently developed a mercury pollution problem (Bodaly and Hecky 1979). Many of the methods used for the Churchill-Nelson study were adaptations of the enclosure and methylation assay methods developed at Clay Lake. For this reason the Churchill-Nelson and the Clay Lake data are directly comparable. In all comparable cases the Churchill-Nelson data support the Clay Lake observations.

III. MERCURY CYCLING IN THE ENGLISH-WABIGOON RIVER SYSTEM

The compelling overall impression of the English-Wabigoon data is of the rapidity of mercury cycling within the river system and the responsiveness of this cycling to short term physical and chemical changes. Geochemical examples of this are presented in Parks et al. (1981). They found a similar relationship at all sampling sites between the concentration of mercury in the surface sediments at a particular site and the concentration of mercury within the water column at that site. Because this mercury partitioning was occurring in a flowing river system, it suggested that equilibrium was established rapidly - within days. The DFO group also examined mercury partitioning within the water column of the enclosures. In less than two days, radiolabelled mercury had partitioned stably into five chemical species. Subsequently the relative abundance of these species remained unchanged as mercury was adsorbed by the bottom sediments (Rudd et al. 1980a and b; Sections 2, 3 and 5). Half-times of the labelled mercury in the water column were quite short (about 20 days) resembling those observed by Parks et al. (1981).

It seems possible that such a rapidly cycling system, could also respond quickly to changes in factors controlling the partitioning between various geochemical compartments and this was found to be the case. Parks et al. (1981) found that increases in water temperature were followed by increases in mercury concentration in water, apparently as a result of desorption of mercury from sediments. We also found that changing the chemical conditions in some of our enclosures, such as by the addition of 100 µg/L Se, reduced the rate of movement of labelled mercury into the sediments (Section 3) Resuspending clay rich sediments in an enclosure had a much different effect. The fine clay sized particles appeared to quickly bind the mercury. Because these particles were too small to sediment, the half-time of the labelled mercury in the water column, which was probably controlled by adsorption rates to the surface sediments, was not altered by this treatment. However, movement of the mercury into the biological compartment (fish, crayfish and zooplankton) was quickly reduced by a factor of ten (Section 2).

The examples presented above demonstrate that mercury in the English-Wabigoon system moves rapidly among the geochemical compartments. They also demonstrate that the rate of movement among the geochemical compartments responded quickly to physical and chemical changes. Further, as will be discussed below, movement from geochemical to biological compartments was also responsive to perturbation. This is important from the point of view of mercury amelioration since a slowly cycling and/or unresponsive system would be very difficult to treat.

Within the biological compartment mercury concentrations might be expected to respond rapidly to changes in the following general control factors: 1) the rate of supply of methyl mercury to fish including the rate of microbial mercury methylation and the availability of methylated mercury for bioaccumulation; 2. the efficiency of mercury bioaccumulation by fish from food and water; and 3. fish growth rate. Fish mercury concentrations have been thought to be negatively correlated with rate of growth (e.g. Beijer and Jernelov 1979). These factors were investigated in this study with the following results.

Supply of methylmercury to fish: Rates of methylmercury production were found to be responsive to several factors. For instance mercury methylating activity in sediments was directly related to mercury concentration over several orders of magnitude of concentration (Fig. 1). This concurs with the observations of Parks et al. (1981) which showed that methyl mercury concentrations in water and fish at a particular sampling site on the river system were related to local total and methyl mercury concentrations found in the water and nearby surface sediment. Because this is a flowing system the methyl-inorganic relationships must have been set up within days.

Another controlling factor that can act with or independently of mercury concentration is the rate of microbial activity. We found that methylation rates in the Clay Lake sediments could be increased by three orders of magnitude by the addition of bacterial food which stimulated microbial activity (Section 6). Using the same methodologies Hecky et al. (unpub data) found recently that methylation rates in surface sediment of samples taken from the Churchill-Nelson River system varied by three orders of magnitude. These differences appeared to be related to differences in rates of microbial activity and not to total mercury concentration. At Southern Indian Lake Hecky et al. also found that increasing microbial activity by the addition of sphagnum moss to an enclosure resulted in measured increases in methylation rate in the water column and surface sediments as compared to controls. Ultimately this led to fish mercury concentrations in the sphagnum enclosure which were 30 times higher than in the control enclosures. Similarly, at Clay Lake we concluded that stimulation of primary productivity, which in turn increased the rate of supply of substrate to bacteria, caused increased methylation rates and an increased rate of supply of methyl mercury to fish (Section 5). It is also interesting that Clay Lake was the only lake of five examined that had a detectable methylation rate in the water column (all five lakes have detectable rates in the sediments; Section 6 and unpublished data). Clay Lake was also the most productive lake examined (Section 5).

Presence or absence of oxygen was also found to quickly affect methylation rates which were usually orders of magnitude higher in the absence of oxygen (Table 1). Similarly, Parks et al. (1981) found that methyl mercury concentration increased in the Wabigoon River upstream from Clay Lake during a period of anoxia.

Sulfide is generally thought to act as an inhibitor of mercury methylation (Section 6). However, even though the anoxic surface sediments of Clay Lake were high in sulfide, bacteria in these sediments methylated mercury as rapidly as in non-sulfide containing oxic sediments (Section 6). This lack of a sulfide effect was confirmed by progessive increases in methyl mercury concentrations with time in anoxic water overlying sulfide containing sediments in the western basin of Clay Lake (Section 6; Parks et al. 1981). The reason for this may be that an excess of ferrous iron in the surface sediments which bound sulfide as FeS and limited its effectiveness as a mercury sequestering agent (Section 6).

The addition of uncontaminated clay rich sediments to an enclosure reduced the supply of mercury to fish and other biota by an order of magnitude (Rudd and Turner (in prep.(b)). This was probably caused by binding of inorganic and/or methyl mercury to the suspended sediment making it less available for methylation and/or bioaccumulation both in the water column and surface sediments of the enclosure. At Southern Indian Lake (Hecky et al. unpublished data) presence of clay rich sediment in an enclosure, reduced mercury accumulation in fish by a factor of three. Both of these enclosure experiments agree with an experiment done at the inflow and outflow of Clay Lake (Rudd and Turner, in prep(b)). During this experiment methyl mercury concentrations were higher at the outflow then the inflow, even though total mercury was lower in concentration at the outflow. This corresponded with a lower suspended sediment load at the outflow, suggesting that inorganic mercury at the outflow was more available for methylation. Also, caged fish bioaccumulated mercury faster at the outflow than at the inflow (Rudd and Turner, in prep.(b)) suggesting that the mercury was more available at lower suspended sediment concentrations. In support of these observations Parks et al. 1980 and Jackson et al. 1980 observed that the ratio of total to methyl mercury and the suspended sediment load decreased with distance from Dryden (Fig. 1). This also suggests mercury methylation concentration of suspended particulate material is lower.

Bioaccumulation efficiency: A second factor which controls fish mercury concentration is the efficiency with which fish bioaccumulate methylated mercury. We found that this was also quickly responsive to deliberate manipulation. For instance, within two weeks of selenium addition (1-100 μg Se/L) to the water column of enclosures rates of mercury bioaccumulation by fish and other biota were detectablely decreased (Rudd et al. 1980b and Sections 3 and 4). The decrease in rate of mercury bioaccumulation (up to 2-fold) was a function of selenium concentration of the fish food. Selenium interfered with absorption of mercury from the alimentary tract (Section 4). In addition to fish this selenium effect was observed in the crayfish and some species of insects (Rudd et al. 1980b; Section 3; B.E. Townsend unpub. data). A food chain response was also observed, in which the selenium effect was more pronounced in predatory fish than in other fish (Section 4). Microbial mercury methylation rates in surface sediment samples were not reduced by the selenium concentrations used in these experiments (Furutani unpub data).

Fish growth rate: It has been hypothesized that an increase in fish growth rate is a third controlling factor that would decrease fish mercury concentration by dilution of bioaccumulated mercury (e.g. Beijer and Jernolov 1979). Contrary to this hypothesis we found that increasing fish growth rate by stimulation of primary production resulted in either stable or slightly increased fish mercury concentrations even though the pH increased in the high productivity enclosures (Section 5). Apparently methyl mercury production in the ecosystem responded as quickly as fish growth rate to an increased supply of food (plankton) which offset the effect of increased growth rate. This experiment has since been repeated at Southern Indian Lake (Hecky et al unpub data) with the same overall result.

Two other observations have been made that are consistent with the dynamic nature of mercury cycling in the English-Wabigoon system. It has previously been thought that the sole site of mercury methylation in lakes is in the sediments (Section 6). However in addition to methylation in sediments, we also found methylation in the water column and in the intestinal contents of all five fish species tested (Sections 6 and 7). Importantly mercury methylated in either the water column or the gut is immediately available for transfer across the gills or gut wall and into fish muscle. Thus it appears that mercury can be methylated in the aquatic environment wherever there is microbial activity.

The examples presented consistently demonstrate the rapidity of mercury cycling in the English-Wabigoon system. They also show that the rate of mercury movement among compartments within the ecosystem (and into fish) can be quickly altered. The key to a successful amelioration strategy is to understand this system to the extent that key processes responsible for elevated mercury concentration in fish can be identified and manipulated in a predictable way (i.e. what is the achilles heel of mercury cycling?). We consider that the rate of supply of mercury to the fish was the most amenable to manipulation since we observed the largest changes (often orders of magnitude) in the shortest time periods (Sections 2,6; Fig. 1). Attempts at reducing fish bioaccumulation efficiency by selenium additions (Sections 3,4) were also successful, although fish mercury bioaccumulation was reduced less dramatically (by up to 2-fold). Altering the fish mercury concentration by changing the fish growth rate had the least effect on fish mercury concentration probably because of off-setting changes within the ecosystem (Section 5).

Methyl mercury does not cycle quickly through fish. Lockhart et al. (1972) observed half times in pike of about two years. Thus changes in factors controlling rates of methyl mercury production and accumulation by fish would have a greater affect on younger, faster growing fish than on older, slower growing fish. For this reason an overall amelioration strategy should include treatment of one or more of the factors controlling production and accumulation plus removal of older fish.

IV. COMPARTMENTALIZATION OF MERCURY CYCLING

Up to this point in the discussion of mercury cycling in the English-Wabigoon system we have dealt only with those parts of the cycle that are within the water column and near the sediment-water interface (compartments 1 and 2 of Fig. 2). This is because it appears that the older deeper sediments below the mixing depth (Compartment 3 of Fig. 2), which contain most of the mercury (Parks et al. 1981; Armstrong and Hamilton 1973; Jackson and Woychuck 1980), are not presently the most important sources of total and methyl mercury to the biota. This conclusion is based on the following observations:

1. Locations on the River system that have large quantities of mercury in deep sediments (e.g. the Wainwright Dam, and the eastern and western basins of Clay Lake) are not sources of total or methyl mercury. In fact Clay Lake is a net sink for total mercury (Parks et al. 1981).
2. The quantity of methyl mercury presently being transported downstream (Parks et al. 1981) is in excess of the estimated quantity of mercury required to maintain the present fish mercury concentrations. Thus there is no reason to think that movement of methyl mercury from deep sediments contributes significantly to the current problem.
3. Parks et al. (1981) have found that total and methyl mercury concentrations in the water and biota at a particular sampling site were related to local surface sediment mercury concentrations.
4. Mercury concentrations of Clay Lake surface sediments have generally decreased since the initial observation of 1971 (Armstrong and Hamilton 1973; Rudd et al. 1980b; Parks et al. 1981). Recent sediment profiles have peaks in mercury concentration up to several centimeters below the sediment-water interface (Rudd et al. 1980b; Parks et al. 1981) indicating that surface sediment concentrations have been gradually decreasing by deposition of cleaner sediments. Crayfish, which live at the sediment-water interface, have responded to this change with progressively decreasing mercury concentrations during the past few years.(A.L. Hamilton, unpublished data).
5. Rudd et al. (Section 2 1980b) found that fish in an enclosure with a sealed plastic bottom which contained compartments 1 and 2 of Fig. 2 (i.e. the water column and a layer of organic rich material which accumulated on the enclosure bottom during the experiment), bioaccumulated mercury an order of magnitude faster than fish in an enclosure with natural lake sediments. It was concluded that suspension of deeper clay rich sediments and more rapid removal of Hg from the water by the clay rich sediments (i.e. those in compartment 3 of Fig. 2) in the control enclosure reduced the rate of bioaccumulation by the same mechanism discussed in

Section 2. Similar observations have since been made in an enclosure experiment at Southern Indian Lake.

6. Using techniques adapted from those described in section 6, rates of mercury methylation in sections of sediment cores were found to be highest near the sediment-water interface. Methylation rates decreased progressively with depth in the cores (Rudd unpub. data).

These observations show that the present mercury contamination of fish in the English-Wabigoon system is not a consequence of mercury buried in the deep lake sediments. Instead it is related to present water and surface sediment mercury concentrations. These concentrations are controlled by continuing mercury discharges from the Great Lakes Forest Products Mill and by erosion and desorption of mercury from the river surface sediments particularly in the stretch of river between Dryden and Clay Lake (Parks et al. 1981).

Because mercury buried deep in lake sediments of the river-lake system is not the source of the present problem, it follows that this mercury should be left undisturbed. It also follows that amelioration procedures directed primarily towards mercury in deep lake sediments (such as dredging and harrowing) and which neglect present mercury loading to the water column and surface sediments will be unsuccessful.

V FEASIBILITY OF SUGGESTED MERCURY AMELIORATION PROCEDURES

For the reasons discussed in IV amelioration strategies such as the harrowing of lake sediments to dilute sediment mercury concentrations, or a single application of clean clay on the lake surfaces would be unsuccessful if these were the only treatments undertaken. A sequence would probably develop similar to that shown in Fig. 3 for a single clean clay application to lake sediments. The present sediment mercury concentration profiles (Fig. 3a) which have a peak in concentration below the sediment water interface would initially be favorably altered (Fig. 3b) by the reduction of surface mercury concentrations. Concurrent transitory increases in suspended material would also be favorable (section 2). However, continued loading to the system particularly from the erosion and desorption of mercury from surface sediments of upstream stretches of river would finally result in a sediment mercury profile with surface mercury concentrations similar to the present situation (Fig. 3c). The end result would probably be a mercury pollution problem similar to the present situation.

Treating the system or specific sites with sulfide would also probably not be successful. Sulfide could be effective at binding mercury in deep anoxic sediment but these sediments are not presently the problem. Treatment of surface sediments, which are continuously or periodically oxic, would be questionable because of sulfide oxidation. Further, even under anoxic conditions surface sediment methylation was not inhibited by the presence of bound sulfide (section 6).

Reduction of Mercury Loading: Further reductions of mercury loading into the system would improve the situation. Rates of mercury methylation in lakewater and sediment are very responsive to changes in mercury concentration (e.g. Fig. 1). Recent further decreases in mercury discharge from the G.L.F.P. mill should help the problem (Jackson et al. 1981; Parks et al. 1981). Desorption and erosion of mercury from stretches of river, particularly between

Dryden and Clay Lake, continues to be a major source of mercury to the river-lake systems. Unlike dredging of lake sediments removal of river sediments from the Wabigoon River between Dryden and Clay Lake is desirable although it is probably not economically feasible. Hydraulic flushing (Parks et al. 1981) followed by burial in Clay Lake and Ball Lake sediments might be a possible method.

Selenium as Mercury Ameliorating Agent: The addition of selenium (as selenite) to the river system was found to be a promising future ameliorating strategy. When 100 µg Se/L was added, the rate of fish mercury accumulation was reduced by a factor of two (Section 3; Rudd et al. 1980a). The effect was both dose and species dependent. For example white sucker was the only nonpredatory fish species that showed a significant reduction of mercury bioaccumulation at 1 µg Se/L (Section 3). The selenium effect was apparently transmitted via the food (Rudd et al. 1980a; Sections 3,4). Elevated concentrations of selenium in water only were not as effective at reducing mercury concentration (Sections 4 and 8). Food chain magnification of this selenium effect was also observed (Section 4). At 10 µg Se/L reduction of mercury accumulation was observed in predatory but not in most other fish (Sections 3,4). When Sections 3 and 4 are considered together they suggest that long-term exposure of this system to selenium at concentrations below 10 µg/L would reduce mercury concentrations in predatory fish.

Selenium is also known to reduce the toxicity of methyl mercury to fish consumers (e.g. Ganther and Sunde 1974). In our enclosure experiments the added selenium was bioaccumulated very efficiently by fish (Rudd et al. 1980a;b; Sections 3, 4) demonstrating that its addition would reduce the very high ratio of Hg:Se presently found in the Clay Lake fish (Rudd et al. 1980a).

Both of the ameliorative effects of selenium demonstrated in our enclosure experiment are transmitted via the food chain (Rudd et al. 1980a Sections 3 and 4). This is an important advantage for selenium as a mercury ameliorating agent because the beneficial effects of selenium would be operating in the most active parts of mercury cycle (Compartments 1 and 2 of Fig. 2). Its use as an ameliorating agent would also be economically feasible. The cost of enough selenite for a single application to the river system is estimated to be about 25 K. The necessity of subsequent additions remains to be determined.

Selenium toxicity to members of the food chain is a possible disadvantage which was also studied as part of our research (Sections 3,8). A reported synergistic Hg-Se interaction on carp eggs (Huckabee 1974) was not found in our laboratory tests of rainbow trout eggs (Section 8). Three species of juvenile fish had LC_{50} values for selenite which were at least four orders of magnitude above concentrations anticipated to be necessary for mercury amelioration (Section 8). No selenium toxicity was found in the enclosure zooplankton communities at either 10 or 100 µg Se/L (Salki et al. in prep.). A shift in dominance of phytoplankton species occurred in enclosure experiments carried out at 10 and 100 µg Se/L (Section 3). In addition primary productivity and fish growth was enhanced in the 100 µg Se/L enclosure (Secton 3).

Despite the generally favorable results we do not at present recommend selenium as a mercury ameliorating agent. Answers to several important questions are necessary before selenium could be applied safely to the English-Wabigoon system. These gaps in our knowledge are:

1. The minimum water column and surface sediment concentrations that would be necessary for a long term improvement of fish mercury concentrations should be established. Our data suggest that concentrations below 10 μg Se/L would be effective. However we were unable to obtain more precise information because of the short duration of our enclosure experiments (up to 2 months) and because it was not possible to maintain fish predators in the enclosure ecosystems. Until a minimum effective concentration is established the risk of selenium addition to the most sensitive members of the food chain cannot be assessed. This question could be answered with a multi year whole lake experiment.

2. At the present time it is not known how long a single selenium addition would continue to be effective. Frequent small additions or a continuous slow rate of addition might prove to be the safest and most effective means of application because water concentrations would be minimized.

3. Possible toxic effects if the river system were treated have not been adequately researched. Fish toxicity tests should be extended to include long term chronic exposures of larval to adult fish (Section 8). A study of the minimum concentrations and ecosystem consequences of selenite toxicity to benthic insects, zooplankton, and phytoplankton species should be conducted because certain members of these communities have been found to be the most sensitive species tested. Because microbial and chemical transformations of selenium are known to occur in aquatic environments, production and toxicity of other selenium species should also be studied (Section 8). These tests should be done with English-Wabigoon water to improve their predictability.

Resuspension and deposition of Clay Rich Material as a Mercury Ameliorating Procedure: In our experiments the largest reduction in rates of mercury bioaccumulation by fish and other biota were achieved by the addition of Wabigoon lake sediments to an enclosure. This treatment reduced the rate of mercury bioaccumulation from the water column and surface sediments by an order of magnitude (Section 2 Rudd et al. 1980b). A similar result has also been documented at Southern Indian Lake when rates of fish mercury bioaccumulation in enclosure with and without clay rich sediments were compared (R. Hecky et al. unpubl. data). Resuspension of sediments followed by downstream deposition is an attractive amelioration strategy because it attacks the mercury problem both in the water column and at the sediment-water interface.

Our sediment addition experiment (Section 2) has directly demonstrated the water column and surface sediment effects. Research at Southern Indian Lake and the caged fish experiment carried out at the inflow and outflow of Clay Lake have supported these results (Hecky et al. unpub data, Section 2).

Increasing the load of suspended sediment in the river system would also increase the rate of deposition of inorganic material onto the surface sediments. At the present time Clay Lake sediments consist of an organic rich surface layer, which overlies more consolidated clay rich sediments. An increase in sedimentation rate of inorganic material would probably reduce mercury methylation in the surface sediments in two ways. It would dilute the concentration of recently deposited organic material in the surface sediments. Because this organic material is an important source of bacterial food and because increasing bacterial substrate concentration stimulates mercury methylation (Section 6; Hecky et al. unpub data), in situ methylation rates would probably be reduced. In addition we and others have also demonstrated that methylation rates are a function of inorganic mercury concentration as well as other controlling factors (e.g. Fig. 1). Thus dilution of sediment mercury concentration in surface sediments by increased clean clay deposition would probably also reduce methylation rates. In support of this viewpoint, Parks et al. (1981) found that methyl mercury concentrations in water and small fish at a particular sampling site are strongly related to mercury concentrations of the surface sediments. For these reasons it is concluded that increasing the load of suspended sediments in the English-Wabigoon system would reduce the rate of movement of mercury into the biota both from the water column and from the surface sediments.

Because there is presently continuous mercury input to the river system from desorption/erosion of mercury from surface river sediments, frequent periods of sediment resuspension would be necessary (e.g. throughout each ice free season). If periodic resuspension was not continued as long as mercury input continues the result would be the unfavorable sequence presented in Fig. 3.

A first step in this amelioration approach would be the selection of a suitable source of clay rich substrate. Recent investigations at Southern Indian Lake (R. Hecky unpub. data) have shown that clay rich bank material obtained from above the water line had no effect on the rate of bioaccumulation of mercury when it was added to the water column of an enclosure. However, resuspension of clay rich sediments from the bottom of another enclosure at Southern Indian Lake had the same type of beneficial effect that we found at Clay Lake using sediments taken from the bottom of Wabigoon Lake. Thus the source of this material appears to be crucial. Our present hypothesis is that clay sized particles taken from the bottom of lakes may have been coated with either organic material or sesquioxides of Fe or Mn, which may be responsible for binding mercury and reducing its bioavailability (Jackson and Woychuk 1980). Bank material may not have these coatings or they may be of a different character. The chemical differences between these two types of clay sources are presently under investigation at the Freshwater Institute. In any case it would be prudent to test the efficacy of the material before large scale resuspension commenced.

At the present time the resuspension and downstream deposition of clay rich sediments also appears to be a practical ameliorating strategy since there is an abundance of easily accessible material within the river system. Most likely sources include the sediments of Wabigoon and Eagle Lakes and the sediments of the eastern or western basins of Clay Lake. The river basin between Dryden and Clay Lake also contains deposits of clay rich sediment which might be resuspended by diversion of the river within its channel or by removal of bed rocks sills within this stretch of the river as suggested by Parks et al. (1981).

Filling gaps in our understanding of this amelioration procedure would enable us to be

more precise about a most practical stategy. Information is needed on:
1. The concentration of resuspended sediment in water and surface sediments that would be required to reduce mercury concentration of the biota to acceptable levels. 2. The relative importance of fish mercury bioaccumulation from the water column and surface sediments. For example, if surface sediments were substantially more important for fish mercury bioaccumulation, it might not be necessary to constantly maintain a high suspended load in the water column. 3. Testing the ameliorative efficiency of various clay rich sediment sources should also be undertaken. 4. The risks involved in resuspension of various ratios of clean and mercury rich sediments should be assessed. All of the above questions could be addressed by enclosure experiment similar to those recently completed at Clay Lake. In addition a survey of methylating activity versus percent inorganic material in surface sediment would result in a better understanding of concentrations of clay minerals that would be necessary to significantly reduce the rates of mercury methylation. Such a survey would be supportive of the proposed enclosure experiments.

This further research would be very useful in predicting the effects of sediment resuspension on the ecosystem. For instance, if we knew more precisely the necessary concentration of suspended sediments and the duration and frequency of resuspension that would be required, the effects on primary productivity in the system should be predictable (Hecky and Guildford in prep). In addition, fish productivity effects of increased suspended sediments following flooding of Southern Indian Lake should give us some information on the effects that resuspension of sediment could have on fish productivity in the English-Wabigoon system (R. Hecky pers. comm).

To obtain maximum improvement in the present mercury pollution problem of the English-Wabigoon system a combination of procedures is recommended. For example an overall solution might include resuspension of clay rich sediments, plus further reductions in mercury loading to the system from the mill and surface river sediments between Dryden and Clay Lake. These measures could be followed by removal of the larger fish with the highest mercury concentration after reductions had been observed in rate of mercury bioaccumulation by the biota.

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Table 1. Mercury methylation rates were usually orders of magnitude faster when surface sediments from ELA lakes were incubated under nitrogen or under air but without shaking than when the same sediments were shaken to promote dissolution of oxygen from the air. A slurry or one gram dry weight of sediment was incubated for 18 hours in a 250 ml ground glass stoppered bottle in the presence of 10 uCi of 1 uCi/ug ^{203}Hg. Analyses of $CH_3\,^{203}Hg^+$ produced during incubation were done as described in section 6.

Date 1980	Lake	Incubation Conditions		
		Static with Air dpm/g/hr	Shaken with Air dpm/g/hr	Shaken with Nitrogen dpm/g/hr
May 6	114	13,900	0.00	—
May 16	239	113,000	118	211,000
May 26	114	33,000	34.0	—
June 25	114	20,800	10,600	20,900
July 15	223	45.0	37.0	40.0
Sept. 6	114	439	-	1,120
Oct. 10	114	5,600	53.0	5,800

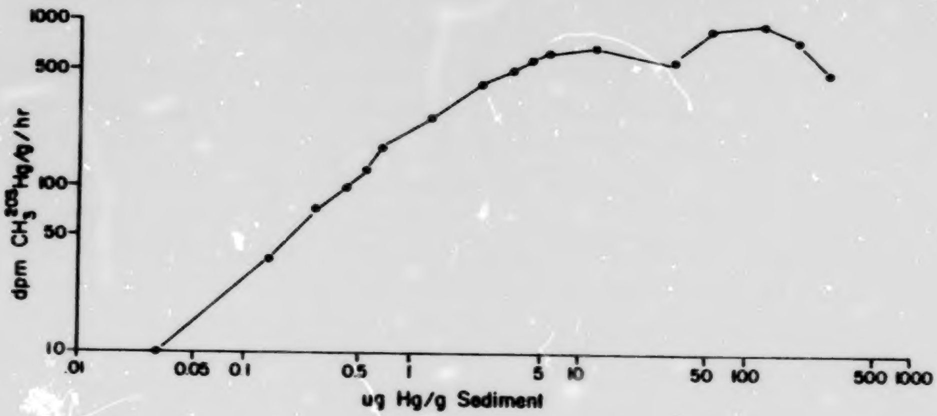

Fig. 1. Influence of inorganic mercury concentration on methyl mercury production rate. Aliquots of a surface sediment sample were incubated for 18 hours in 250 ml ground glass stoppered bottles in the presence of increasing concentrations of 203-labelled mercury.

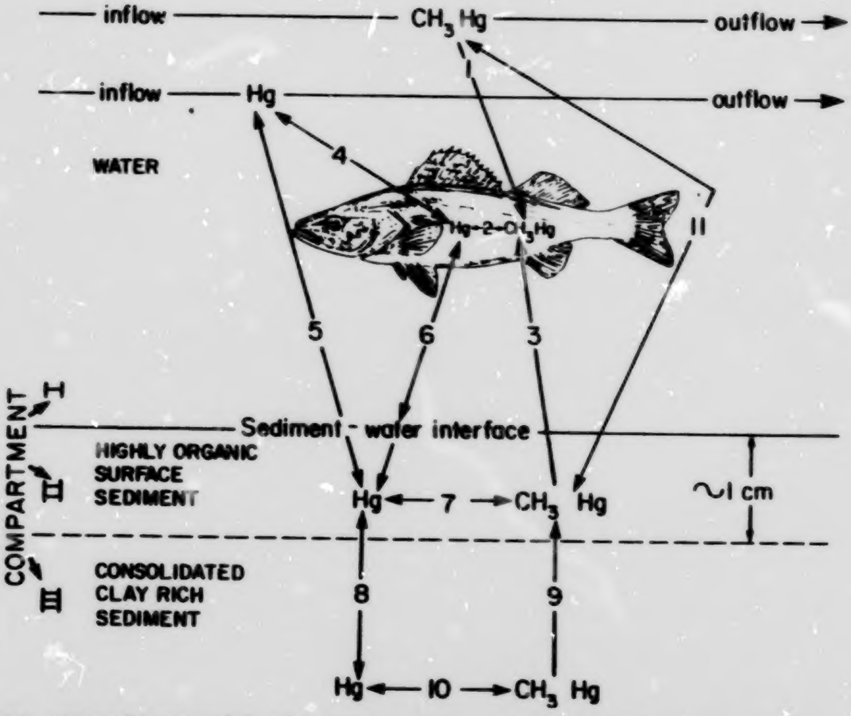
inflow
CH_3Hg
outflow
inflow
Hg
outflow
WATER
4
1
Hg-2-CH_3Hg
11
5
6
3
COMPARTMENT
I
Sediment - water interface
HIGHLY ORGANIC SURFACE SEDIMENT
II
Hg
7
CH_3 Hg
~1 cm
CONSOLIDATED CLAY RICH SEDIMENT
III
8
9
Hg
10
CH_3 Hg

Fig. 2. A three compartment model of mercury cycling in the English-Wabigoon river system showing interconnecting pathways of mercury movement from water and food into fish. Compartments 1 and 2 cycle mercury most rapidly and are closely interrelated. Pathways 1, 2 and 3 are thought to be the major contributors of methyl mercury to fish. Deeper more consolidated clay rich sediments (compartment 3) which contain large quantities of mercury in some locations do not contribute substantially to the present mercury pollution problem.

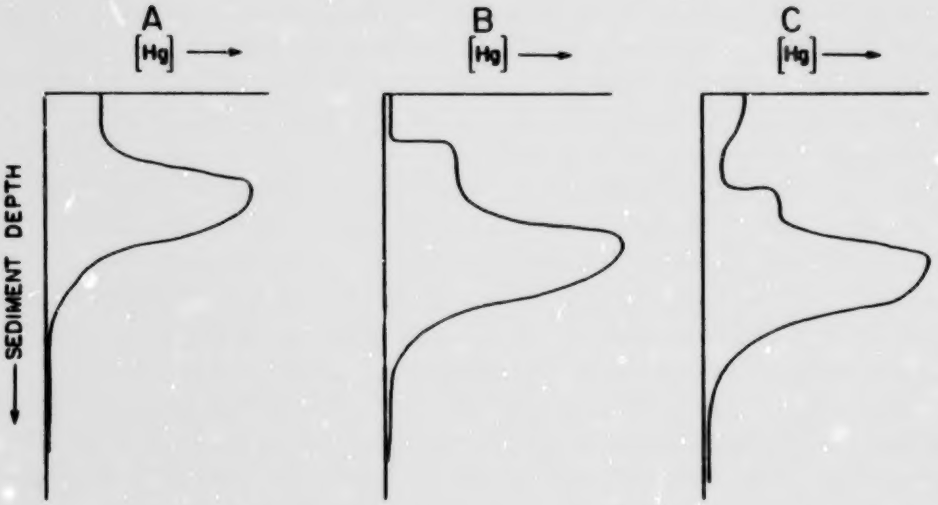

Fig. 3. A schematic representation of a present mercury concentration profile in the English-Wabigoon river sediments (a). The profile after a single addition of clean clay (b). The shape of the profile several years after the clay addition (c) when deposition of new contaminated surface sediment from upstream of Clay Lake would result in a mercury pollution problem similer to the present situation.

2. INHIBITION OF MERCURY AND SELENIUM BIOACCUMULATION FROM WATER AND SURFACE SEDIMENTS OF LARGE IN SITU ENCLOSURES BY THE ADDITION OF SUSPENDED SEDIMENTS

J. W. M. Rudd and M. A. Turner

INTRODUCTION

Suspended sediments are thought to play an important role in the bioconcentration of toxic substances (Karichkoff and Brown 1978; Gibbs 1973; Hem 1976; Tessier et al., 1980; Popp 1980). They have often been considered as vectors which are capable of moving pollutants from their sources to distant locations where the toxic substances can be accumulated by aquatic biota. At neutral pH the sediment borne pollutants may be associated with particulate or dissolved organic materials, clay mineral, or organic and inorganic (usually Fe and Mn) coatings on the surfaces of clay particles (Jackson et al., 1978; Jackson 1979; Andersson 1979; Andersson 1970 cited in Andersson 1979; Jonasson 1970).

Binding of pollutants such as mercury by clean suspended sediments may also have a beneficial effect on mercury concentration of the biota by limiting its availability for methylation and/or bioaccumulation. Because both of these biological processes occur in the water column and in the sediments (section 6, 7; Topping and Davies 1981; Armstrong and Scott 1979; Huckabee et al., 1979), suspended sediments might have a beneficial effect both while they are water borne and after they are deposited onto the sediment-water interface.

These possibilities were examined during 1978 and 1979 in the mercury contaminated English-Wabigoon River system (Armstrong and Hamilton 1973). We carried out ecosystem experiments in large enclosures located in Clay Lake, which is the first major reservoir of the system (Rudd et al., 1980a and b). These experiments were designed to test the effects of suspended sediments on mercury bioaccumulation from both the water column and surface sediments which have been identified as the major present sources of mercury for fish in this river system (section 1).

In addition, the effect of suspended sediments on movement of selenium through the ecosystem was investigated. This was done because of the known beneficial interactions of mercury and selenium (e.g. Rudd et al., 1980b; sections 3,4 Ganther and Sunde 1979); because selenium addition to the river system is being investigated as a mercury ameliorating technique (sections 3, 4, 8, 9) and because mercury and selenium are released in large quantity into the atmosphere during coal combustion (Klein et al., 1975).

METHODS

Two separate experiments were conducted in 10-meter diameter, 2 m and 1.5 m, deep cross-laminated polyethylene enclosures during the summers of 1978 and 1979 respectively. Construction of enclosures was similar to that described in Rudd et al. (1980 a,b) except that most of the enclosures had water-tight polyethylene bottoms. They were situated in a sheltered bay of Clay Lake, north-western Ontario (Armstrong and Hamilton 1973). The plastic bottom enclosures were filled over a three day period with Clay Lake epilimnion water. Pumps were moved repeatedly from enclosure to enclosure to ensure that water and plankton in all the enclosures was similar.

The 1978 experiment consisted of a control enclosure with a bottom of natural lake sediments (Table 1) and a test enclosure with a sealed plastic bottom which prevented sediment resuspension. The 1979 experiment consisted of three enclosures with sealed plastic bottoms. Sediment was added to the water column of one enclosure (suspended sediment enclosure), the two other enclosures were controls.

Enclosure Treatments

On day zero of the experiments (July 15, 1978; June 4, 1979) each of the enclosures received approximately 6.0 mCi^{203}Hg(NO$_3$)$_2$ (approximately 15 ngHg/L was added as carrier and about 1.5 mCi of H$_2$^{75}SeO$_3$ (New England Nuclear). A single addition of foodgrade sodium chloride was made to each enclosure to check for enclosure leakage. Resulting Na^+ and Cl^- concentrations were approximately twice pre-addition levels, as determined by atomic adsorption spectrometry (Stainton et al. 1977). No leakage was detected during the course of either of the experiments.

The control enclosures and the 1978 plastic bottom exclosure received no other chemical additions. For the 1979 experiment, sediment was obtained from the central basin of Wabigoon Lake which is upstream of Clay Lake and is not mercury contaminated. Care was taken not to include the surface layer of recently deposited organic material. Sediment was added to the third enclosure on three occasions (Table 2). The first addition was approximately 18 Kg dry weight of Wabigoon Lake sediment and the second and third additions were about 12 Kg each. On each occasion wet sediment (59% water) was suspended throughout the water column of the suspended sediment enclosure by dispersing it into the wake of an electric outboard motor. Sediment addition continued until the Secchi depth was 20 cm. This material was largely composed of silt and clay sized particles (Table 1). The sediment additions did not detectably increase mercury concentrations in the water of the enclosures.

Radioactive Sample Analyses

The mercury isotope was added as Hg^{2+} because this is the chemical species which is bacterially methylated. Selenium was added as selenite because it is the most probable chemical species to be added as a mercury ameliorating agent (section 1). The single pulse addition of these chemical species, which were radioactively labelled, enabled us to follow the movement of the labelled atoms through the ecosystem and to determine the effect of an experimental manipulation (e.g. addition of Wabigoon Lake sediment) on their movement. Conclusions were drawn by comparing rates of movement of the isotopes through the ecosystem in the test enclosures as compared to the controls.

It should be noted that the Hg and Se added is not assumed to have come into equilibrium with natural Hg and Se during the course of the experiment. Rather, we were breaking into the biogeochemical cycle of these elements by introducing the chemical species that were of particular importance to us. By using radioactive isotopes we were able to follow these additions throughout the cycle.

The advantages of using isotopes for these experiments were threefold: 1) analytical sensitivity, 2) in situ Hg and Se concentrations were not radically altered, 3) a definite time for the beginning of the experiment could be established.

Biological and water samples were analyzed for ^{203}Hg and ^{75}Se exactly as described in Section 5. Water samples were filtered and analyzed for the concentrations of Hg and Se isotopes associated with particulate material > 0.45 um. The filtrate was passed through cation-anion exchange resins and an activated charcoal column to separate ionic and organic fractions. A portion of the ^{203}Hg was not associated with any of the above fractions and was assayed after removal by precipitation as HgS (Rudd et al. 1980b and section 5).

Five or six clams (Anodonta sp.), crayfish (Orconectes virilis) and pearl dace (Semotilus margarita) were analyzed for isotope activities on each sampling date. The dace were free swimming while the crayfish and clams were confined to cages placed on the bottoms of the enclosures. The crayfish were fed an excess of white sucker flesh with a mercury concentration of about 0.2 μg Hg/g.

The isotope bioaccumulation data are presented as ratios in which the lognormal means of the isotope activities per gram wet weight of the test samples were divided by the mean of the control activities.

Bioaccumulation of both isotopes was also followed in zooplankton, i.e. particulate material greater than 83μm. Each sample comprised zooplankton collected from three Schindler trap hauls (Schindler 1969) taken at 0.25, 0.75 and 1.25 m depth. Zooplankton activities were calculated on a dry weight basis.

Movement of ^{203}Hg and ^{75}Se into the haptobenthic community was also followed by assaying the haptobenthos colonized on polyethylene strips hung from the surface to a depth of one meter in the enclosures. After assay of its radioactivity, the haptobenthos was dried, scraped from the polyethylene and weighed. These strips were uncolonized when they were suspended in the enclosures. All isotope data were decay corrected to spike day, day zero of the experiment.

Other Analyses

During 1979, weekly estimates of cloudless primary productivity were done using the ^{14}C incubator technique (Fee 1973 a,b; Shearer 1976 a,b) as described in section 5.

Total and methyl mercury concentrations in water were analyzed according to methods described in Furutani and Rudd (1980).

Total mercury concentrations in fish were analyzed by the method of Armstrong and Uthe (1971). Total suspended solids were estimated as described in Stainton et al. (1977) except that samples were filtered with 0.45 μm membrane filters instead of glass fiber filters. In addition water samples were taken on a fixed schedule and analyzed for total dissolved phosphorus particulate carbon and phosphorus, and dissolved organic carbon, as described by Stainton et al. (1977).

RESULTS

1978 Experiment

Wave action on the walls of the enclosures continually resuspended bottom sediments in the control enclosure maintaining the Secchi depth within a range of 0.7-1.0 m. Within two weeks, Secchi depth in the enclosure with a sealed plastic bottom was greater than the depth of the enclosure (2m) and remained at greater than 2m depth for the duration of the experiment (56 days). The water column half-time of ^{203}Hg in the enclosure with a plastic bottom was twice as long as in the control enclosure (36 vs 18 days; Rudd et al. 1980b). Labelled mercury was bioaccumulated by pearl dace 8-16 times faster in the plastic bottom enclosure than in the control enclosure with natural sediments and more suspended particulate material (Fig. 1). At the end of the experiment mercury concentration of crayfish were 15 times higher in the plastic bottom enclosure than in the control enclosure (data not shown).

Selenium-75 bioaccumulation was also reduced by the presence of bottom and suspended sediments. Pearl dace activity was 2.0-9.5 times lower in the control enclosure (Fig. 1) and crayfish ^{75}Se bioaccumulation was also about 10 times lower in the control enclosure (data not shown). In the absence of sediments, in the plastic bottom enclosure there was no detectable loss of ^{75}Se from the water during the experiment (Rudd et al. 1980b). The ^{75}Se water column half-time in the control enclosure was 56 days (Rudd et al. 1980b).

1979 Experiment

Secchi depth in both control enclosures increased from 0.8 to 1.5 m between days -9 (i.e. 9 days before isotope addition) and day 8 (Fig. 2), and then remained at about 1.5 m (1.46 ± 0.24, n=26) for the remainder of the experiment. The enclosure to which sediment would be added tracked the controls until the first sediment addition on day -3, which reduced the Secchi depth to 0.2 m. Secchi depth increased linerally until day 8 when a second addition of sediment returned the Secchi depth to 0.2 m. Another addition was made on day 22 when the Secchi depth had increased to 0.9 m. The average Secchi depth of the suspended sediment enclosure after the first clay addition was 0.52 (± 0.20, n=20). During the same time period total suspended solids in the control enclosures were 2.0 mg/L (± 0.0, n=4). Total suspended solids (TSS) were measured twice in the suspended sediment enclosure when the Secchi depth was 0.3 m. On these occasions TSS were 13 and 18 mg/L (dry weight).

The enclosures were functional ecosystems in which fish growth was supported by phytoplankton, haptobenthic and zooplankton production. The enclosures were very similar biologically. Maximum photosynthetic rates did not vary significantly among the enclosures but ranged from 1 to 5 mgC/m^3/hr during the course of the experiment. Haptobenthos accumulated on the polyethylene strips and on the enclosure walls. The zooplankton community maintained its biomass at approximately 0.15 mg/L (dry weight) in all the enclosures throughout the experiment. Pearl dace grew in all of the enclosures, mean weights increasing by 12% in the controls and 10% in the suspended sediment enclosure.

The addition of sediment had no effect on the water column residence time of either ^{203}Hg or ^{75}Se (Fig. 3). Activities of ^{203}Hg decreased by 45% during the course of the experiment and did not appear to have stabilized at the end of the experiment. During the experiment ^{75}Se activity in water decreased by only about 10%, reaching apparently stable values (Fig. 3).

Although there was no overall effect of sediment addition on total activity of ^{203}Hg in the water samples (Fig. 3), there was a significant increase in the percentage of ^{203}Hg on particulate material in the suspended sediment enclosure with a corresponding decrease in the quantity of ^{203}Hg in the other fractions (Table 3). On the last day of the experiment a fourth sediment addition was made to examine the short term effects of new particulate on the partitioning of the isotope. No discernable changes from the overall averages presented in Table 3 were observed in samples taken just before and after the sediment addition.

The fact that loss of ^{203}Hg from the water was not affected by the three sediment additions, but the percentage of ^{203}Hg on particulate material increased, leads us to conclude that most of the ^{203}Hg was associated with particles which were either permanently suspended or sedimenting very slowly. This is confirmed in Fig. 2 where progressive increases in Secchi depth, because of sedimentation of larger suspended sediment particles, did not affect the concentration of ^{203}Hg in the water of the suspended sediment enclosure (Fig. 3). The percentage of ^{203}Hg on suspended particulate material (43%; Table 3) is an underestimate because some clay sized particles were observed to have passed through the 0.45 um membrane filters. Conversely, one or more of the "dissolved" fractions will be overestimated because their isotopic activities were determined using filtered water.

Long term partitioning of ^{75}Se was not affected by increased suspended sediment concentrations (Table 3). As in other experiments (Rudd et al. 1980a,b; sections 3), ^{75}Se in both the suspended sediment and control enclosures was primarily associated with the particulate fraction (≈55%) at the beginning of the experiment. This changed rapidly during the first week of the experiment so that after day 9 about 55% of the ^{75}Se in all enclosures was associated with the organic fraction (activated charcoal). There may have been a short term affect of sediment addition on the partitioning of ^{75}Se. Immediately after the fourth sediment addition on the last day of the experiment the percentage of ^{75}Se in the organic fraction increased from 57% to 75%. This ^{75}Se was drawn entirely from the ionic fraction which decreased from 32% to 14% of the total ^{75}Se activity.

The areal activity of ^{203}Hg of the haptobenthos (cpm/cm^2) was initially lower in the suspended sediment enclosure than in the controls (Fig. 4). By day 22 and at the end of the experiment ^{203}Hg areal activities in all of the enclosures were similar. Haptobenthos biomass, which includes living organic and inorganic particulates, peaked on day 22 in all of the enclosures. On that sampling date biomass was four times higher in the suspended sediment enclosure than in the controls. Therefore at peak biomass ^{203}Hg activities per gram of haptobenthos were reduced four fold in the sediment enclosure.

The areal activities of ^{75}Se in the haptobenthos followed the same pattern as ^{203}Hg (Fig. 4), although the areal activity present on day 22 was more than twice as large as the controls. In this case the ^{75}Se per gram of biomass was reduced by a factor of two in the suspended sediment enclosure because the areal biomass was four times higher in this enclosure.

Time course data of the movement of both mercury and selenium into the zooplankton, crayfish and pearl dace in the control enclosures have been presented in Fig. 3 of section 5. The patterns of bioaccumulation of both isotopes were very similar in both control enclosures.

Zooplankton activities peaked early and then progressively declined. They appeared to follow the declining activities in water which would be expected of organisms with short life spans that accumulate isotope from water. Pearl dace activities plateaued after 17 days of exposure. Both ^{203}Hg and ^{75}Se in crayfish increased continuously throughout the experiment. The excellent reproducibility of the control enclosures (Fig. 3 of section 5) indicates that enclosure to enclosure variability was not a factor in interpreting the large differences in isotope activities of biota between the controls and suspended sediment enclosures.

The added sediment substantially reduced bioaccumulation of mercury by the zooplankton (Fig. 5), crayfish (Fig. 5), clams (Table 4) and pearl dace (Fig. 6). Zooplankton activities were lower by about 80% while those in whole bodies of crayfish, clams and pearl dace were lower by 85-90%. Movement of ^{203}Hg into pearl dace muscle was reduced to an even greater extent. By the end of the experiment mercury activities were 95% lower in the suspended sediment enclosure than in the controls (Fig. 6).

Selenium bioaccumulation was also reduced by sediment addition, but to a smaller extent (Fig. 5; Fig. 6, Table 4). Selenium bioaccumulation by zooplankton and crayfish and clams was reduced by 50%, 30% and 25% respectively. In whole bodies of pearl dace ^{75}Se activity was reduced by about 40%. At the end of the experiment pearl dace muscle selenium - 75 was reduced 30% compared to the controls.

DISCUSSION

Clay Lake sediments have a surface layer of recently deposited organic-rich material which overlies highly inorganic sub-surface sediment. Mercury methylation and bioaccumulation occurs in both sediment layers and in the overlying water (sections 1, 6, 7; Jacobs and Keeney 1974; Olson and Cooper 1974; Topping and Davies 1981; Huckabee et al., 1979; Armstrong and Scott 1979). However, the water column and the organic rich surface sediment layer have been identified as the major contributors of methyl mercury to fish in the English-Wabigoon system (section 1). The deeper inorganic sediments, which may contain high concentrations of mercury, are apparently not contributing significantly to the present mercury levels in the biota (section 1).

The two enclosure experiments described in this section were designed to examine the effects of sediment on bioaccumulation of mercury from both the water column and surface organic-rich sediments. All of the plastic bottom enclosures used during 1978 and 1979 accumulated a surface layer of organic rich material on the enclosure bottoms during the experiments similar to the organic-rich surface layer in the 1978 control enclosure with natural sediments. The 1978 control enclosure additionally contained highly inorganic sediment (Table 1) which was initially on the bottom underlying the surface organic layer and which was partially resuspended during the experiment by wave action on the walls of the enclosure. The presence of inorganic sediments on the bottom of the enclosure with natural sediments caused a two-fold reduction in the water-column half-time of ^{203}Hg as compared to the plastic bottom enclosure (Rudd et al 1980a). The binding of ^{203}Hg by the bottom sediments could partially account for the ten fold differences in mercury bioaccumulation by pearl dace and crayfish between the 1978 plastic and sediment bottom enclosures. Additionally, there was probably reduced bioavailability in the water column because of sediment resuspension.

When inorganic-rich sediment was added directly to the water column in the 1979 experiment, there was no effect on ^{203}Hg water column half-time (Fig. 3). This suggests that the large reduction observed in ^{203}Hg accumulation by the biota (Figs. 4, 5, 6), including a 95% reduction in pearl dace muscle (Fig. 6), must have been a direct effect of suspended sediment. An overall interpretation of both experiments is that binding of ^{203}Hg and/or CH_3 ^{203}Hg by the highly inorganic sediment, either in the water column or on the bottom,is an effective inhibitor of mercury bioaccumulation.

The sedimentation of larger particulate material in the 1979 suspended sediment enclosure resulted in progressively increasing water clarity after each sediment addition (Fig. 2). However this did not affect the water residence time of the labelled mercury (Fig. 3), although mercury bioaccumulation was drastically reduced. This suggests that the mercury in the suspended sediment enclosure was bound to dissolved organics added as part of the wet sediment or to fine particulate material which was either permanently suspended or sedimenting very slowly. Because there was no detectable increase in dissolved or suspended organic carbon concentration in the suspended sediment enclosure as compared to the controls (data not shown), it is possible that the labelled mercury was bound by clay mineral fraction of the suspended sediments. Mercury is known to bind to clay particles by ion exchange reactions and by co-precipitation with organic or inorganics (Fe, Mn) onto the surfaces of clay sized particles (Jonasson 1970). Armstrong and Hamilton (1977) found that mercury was associated primarily with the clay-sized fraction of Clay Lake sediments. In addition Lindberg and Harriss (1977) concluded that Fe and not organics were responsible for the scavenging of mercury after resuspension of sediments in laboratory experiments and Jackson et al. (1982) have concluded that particulate bound mercury was not very available for bioaccumulation. In our experiments the binding of mercury to clay-sized particles in both the water and surface sediments could be one mechanism which reduced the bioavailability of mercury in both the 1978 and 1979 experiments.

Suspended sediment concentrations as measured by Secchi depth were similar in the 1979 suspended sediment enclosure (0.5 ± 0.2, n=20; Fig. 2) and the eastern basin of Clay Lake (0.6 ± 0.1, n=24;Table 5). Total suspended solids concentrations in the suspended sediment enclosure (were ≈16 mg/L at a Secchi depth of 0.3 m). Because the Secchi depth in this enclosure averaged 0.5 m, TSS in the suspended sediment enclosure probably corresponded to the inflow and eastern basin of Clay Lake (≈9 mg/L;Table 5). The western basin of Clay Lake, which has greater water clarity, was more closely approximated by the 1979 control enclosures (Secchi depth 1.46m ± 0.24m, n=26; Fig. 2; Table 5). Thus differences in mercury bioaccumulation by the biota between the control and suspended sediment enclosures are probably a good indicators of the importance of inorganic sediments in controlling mercury bioavailability in the two dissimilar basins of Clay lake. An *in situ* demonstration of this mechanism is given in Figs. 7 and 8 and Table 5. In this experiment finescale and pearl dace were held in cages suspended above the sediments at the inflow and outflow of Clay Lake. During an eight week exposure period there was an increase in mercury concentrations in both fish species caged at the outflow but no detectable change in mercury concentration at the inflow (Fig. 7). The ratio of methyl to total mercury in water samples taken at the outflow was higher than at the inflow (Table 5) and total mercury concentrations were lower (Fig. 8; Table 5). The most obvious differences in water quality were the progressive decreases total suspended solids concentrations from the inflow to the outflow of Clay Lake, coupled with an increase in Secchi depth (Table 5). These data suggest that mercury at the Clay Lake outflow was more bioavailable in terms of both methylation and bioaccumulation probably because of the lower suspended sediment concentrations at the outflow. These observations are in agreement with those of Parks et al. (1982) and Jackson and Woychuk (1980) who observed an increases in the ratios of methyl to total mercury in water with distance downstream from Dryden. The increasing ratios of methyl/total mercury also corresponded to decreasing downstream suspended sediment load.

Inhibition of Selenium bioaccumulation

At low concentrations (10 µg Se/L and below) selenium may reduce the rate of mercury bioaccumulation by fish (sections 3, 4). Selenium is also bioaccumulated efficiently, reducing the Hg:Se ratio in fish flesh which reduces methyl mercury toxicity to the consumer (e.g. Ganther and Sunde 1974). At higher concentration (100 µg Se/L), although selenium continues to have mercury ameliorating potential (Rudd et al., 1980 a & b, sections 3, 4), it may also be toxic to some aquatic invertebrates (section 1, 3). At very high concentrations (1000 µg/L and higher) it is toxic to both invertebrates and fish (sections 1, 3, 8). Because of the ameliorative and toxic properties of selenium an understanding of factors controlling its bioaccumulation is necessary. This information would also be useful in designing mercury ameliorating procedures and assessing of possible benefits and risks involved in atmospheric selenium deposition.

In the 1979 experiment addition of suspended sediment reduced the rate of selenium bioaccumulation by 25-50% in all of the members of the food web tested (Figs. 4,5,6; Table 4). A similar effect was observed in a companion experiment in which increasing the rate of primary productivity decreased selenium concentration of the biota (section 5). In that case selenium was diluted by the increased rate of growth of the organisms. In the 1979 sediment addition experiment the reduction was probably a direct effect of sediment because growth rate of fish, zooplankton and phytoplankton was not significantly different from the controls.

In the 1978 experiment resuspension of sediments in the control enclosure from natural bottom sediments was correlated with a much larger (10-fold) reduction in selenium bioaccumulation by pearl dace (Fig. 1) and crayfish (data not shown). Selenium is known to be predominantly associated with the organic material (Table 2; Rudd et al. 1980; sections 3,5) which may reduce its bioavailability. During the 1978 experiment organic material at the sediment-water interface plus some of the underlying predominantly inorganic sediment was resuspended by wave action on the enclosure walls. During the 1979 experiment predominantly inorganic sediments were added to the suspended sediment enclosure. These observations suggest that resuspension of organic rich sediment may have a much larger inhibitory effect on selenium bioaccumulation than resuspension of predominantly inorganic sediments.

The present Hg:Se atomic ratios of northern pike and walleye in Clay Lake are about 10:1 (Rudd et al. 1980b). Our observations that inorganic sediment addition reduced muscle mercury activity by 95% and selenium activity by only 30%, suggest that the Hg:Se ratio of fish in the English-Wabigoon system could be improved (reduced) by resuspension of highly inorganic sediments. Some improvement in Hg:Se ratios may occur even if selenium is not added to the river system as a mercury ameliorating agent.

Resuspension and downstream deposition of clean sediment as a mercury ameliorating procedure

The English-Wabigoon River system downstream of Clay Lake is presently receiving large amounts of mercury in about equal quantities from both the Great Lakes Forest Products Mill and from desorption/erosion of surface sediments of the Wabigoon River between Dryden and Clay Lake (Parks et al. 1982). These continuous inputs are thought to be maintaining high mercury concentrations in water, surface sediment and are thought to be the cause of continuing high mercury concentrations of biota in the river system (Parks et al., 1982; section 1). As long as these mercury inputs continue a single application of clean sediment to surface sediments of the river system would not be a long term mercury solution (section 1). Water and surface sediment mercury concentrations would probably return to about present concentrations soon after clean sediment application resulting in a mercury problem similar to the present situation. Continuous or periodic resuspension of sediment followed by downstream deposition would probably result in a long term improvement of the mercury pollution.

As demonstrated in this section, sediment resuspension followed by downstream deposition would attack the problem both in the water column and surface sediments, which are the two most important contributors of mercury to the biota (section 1). In the water column and surface sediments resuspended sediments would bind mercury and probably reduce its bioavailability. Further, at the sediment surface, increased deposition of clean, highly inorganic material would dilute concentrations of both mercury and organic carbon (bacterial food). Both of these factors have been found to be positively related to rates of microbial mercury methylation in Clay Lake surface sediments (section 1, 6). In support of our data Parks et al., (1981) have found that methyl mercury concentrations fish are correlated with local water and surface sediment mercury concentration throughout the river system.

A single dredge operating in Wabigoon, Eagle or Clay Lakes would probably be capable of suspending sufficient sediment to increase a typical Wabigoon river flow of (1.8×10^5 m^3/hr) to the average suspended sediment concentrations of the 1979 suspended sediment enclosure. The required rate of resuspension is estimated to be approximately 3 tonnes/hour of wet sediment[1].

Before sediment resuspension could be recommended as a mercury ameliorating procedure several possible problems should be considered. In theory increased suspended sediment load might affect primary productivity and fish productivity in the river system. However, in our 1979 experiment we found no difference in primary productivity and fish growth rate between the suspended sediment and the control enclosures even though total dissolved phosphorus and particulate phosphorus concentrations were increased from 14 to 18 µg/L and 10 to 19 µg/L respectively in the suspended sediment enclosure. Hecky and Guildford (in prep) have found that suspension of sediments in the Churchill-Nelson river system following impoundment affected primary productivity in a predictable manner. These results and the investigations of Bodaly (unpub) on post impoundments effects fish growth in Southern Indian Lake should be useful in predicting effects of sediment suspension on English-Wabigoon system.

If suspension of sediments from a heavily mercury contaminated area is contemplated (e.g. Clay Lake Western basin), a safe ratio of clean to contaminated sediments should be determined. Lindberg and Harriss (1979) have found sediment resuspension resulted in a short term (hours) release of mercury followed by rapid readsorption of the mercury as iron was oxidized in suspension. Their overall conclusion was that resuspension of mercury containing sediments by dredging would not be a problem.

There is also a possibility that mercury attached to suspended particulates could be released downstream under different chemical conditions, such as might occur in response to changes in pH and ionic strength. For example, mercury adsorbed to kaolinite, bentonite, illite and iron oxide at neutral pH is greater than 50% desorbed between pH 4.5 - 5.0 and is at least 75% desorbed at pH 4.0 (Andersson 1979). Although such downstream change in pH are not expected this possibility should be fully investigated.

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[1] Sediment resuspension rate was calculated as follows:

$$\text{Tonnes wet sediment/hr} = \frac{F \times S}{D}$$

F = Typical Wabigoon river flow at Quibell = 1.8×10^5 m^3/hr.

S = Concentration of dry sedimnt required to approximate 1979 suspended sediment enclosure = 30 mg/L.

D = fraction of water in wet sediment = -0.5

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Table 1. Analyses of Clay Lake sediments obtained from outside of the experimental enclosures and Wabigoon Lake sediments taken from the central basin of Wabigoon Lake. Surface organic floc was removed during sampling of the Wabigoon but not the Clay Lake sediments. All analyses are presented on a dry weight basis.

Sample	% sand > 50 μ	% silt 50–2 μ	% Clay < 2 μ	%Carbon	% Nitrogen	% Phosphorus	% Carbonate
Clay Lake (as % of inorganic fraction)	1	47	53	–	–	–	–
Clay Lake (as % of total sediment)	1	46	53	4.0	0.3	0.08	0.5
Wabigoon Lake (as % of inorganic fraction)	9	49	42	–	–	–	–
Wabigoon Lake (as % of total sediment)	9	48	41	2.0	0.2	0.07	0.3

Table 2. Chronology of 1979 enclosure additions

Days After Isotope Addition	Addition
-12 to -10	Enclosures filled.
-10	3 kg NaCl per enclosure yielding final concentrations of 13 mg Na/L.
-3	18 kg. sediment added to the suspended sediment enclosure.
0	5.7 mCi $^{203}Hg(NO_3)_2$ and 1.4 mCi $H_2{}^{75}SeO_3$ to each enclosure on June 4, 1979.
4	60 dace per enclosure at an initial density of 40 kg/ha.
7	12 kg sediment added to the suspended sediment enclosure.
7	18 caged crayfish per enclosure.
9	6 caged clams per enclosure.
22	12 kg sediment added to the suspended sediment enclosure.
30	Fourth sediment addition to examine short term isotope. speciation.
30	Termination of experiment.

Table 3. Partitioning of ^{203}Hg and ^{75}Se in water samples taken from the 1979 control and suspended sediment enclosures. Means (± SD) of five samples are reported.

Enclosure	% Particulate (> 0.45μ)	% Charcoal (organic)	% Ionic	% Unassociated
		^{203}Hg		
Control 1	27.4 (±8.1)	24.9 (±8.3)	14.5 (±5.3)	33.1 (±15.3)
Control 2	26.5 (±4.7)	24.6 (±7.5)	13.4 (±4.8)	35.4 (±11.3)
Suspended Sediment	43.2 (±7.8)	16.1 (±5.0)	11.1 (±6.8)	29.7 (±9.5)
		^{75}Se		
Control 1	23.2 (±16.9)	51.1 (±12.3)	25.7 (±11.5)	-
Control 2	23.9 (±19.0)	55.0 (±14.4)	21.1 (±7.5)	-
Suspended Sediment	23.8 (±16.9)	54.7 (±16.7)	21.5 (±7.2)	-

Table 4. Accumulation of ^{203}Hg and ^{75}Se in the foot muscle of clams in the presence and absence of added suspended sediment. The lognormal mean of five clams is reported for the suspended sediment enclosure and of ten clams for the combined controls.

Enclosure	^{203}Hg (cpm/g ÷x SD)	^{203}Hg as % of controls	^{75}Se (cpm/g ÷x SD)	^{75}Se as % of controls
Combined controls	265 (÷x 1.28)	100	190 (÷x 1.48)	100
Suspended sediment	33 (÷x 1.63)	13	143 (÷x 1.73)	75

Table 5. Secchi depth, total suspended solids, and mercury data at four sites on Clay Lake during the open water season (May-Nov) of 1978.

Site	Secchi depth (m)		Suspended solids mg/l		Total Hg ng/l		CH_3Hg^+ Total Hg	
Inflow	0.53±0.10 (0.54±0.07	n=24 n=9)*	10.4±2.1 (9.2±0.84	n=12 n=5)**	35.3±10.7	n=48	$0.048 \overset{\div}{\times} 1.69$	n=22
Eastern Basin	0.63±0.14	n=24	8.5±3.5	n=12	30.5±14.0	n-46		
Western Basin	1.27±0.42	n=23	2.3±0.38	n=12	19.6 ±9.9	n=35		
Outflow	1.39±0.42 (1.29±0.29	n=24 n=9)*	2.4±0.79 (2.4±0.89	n=12 n=5)**	17.9± 7.4	n=50	$0.10 \overset{\div}{\times} 1.62$	n=22

* sampled weekly during Aug 23-Oct. 18

** sampled biweekly during Aug 30 - Oct. 25

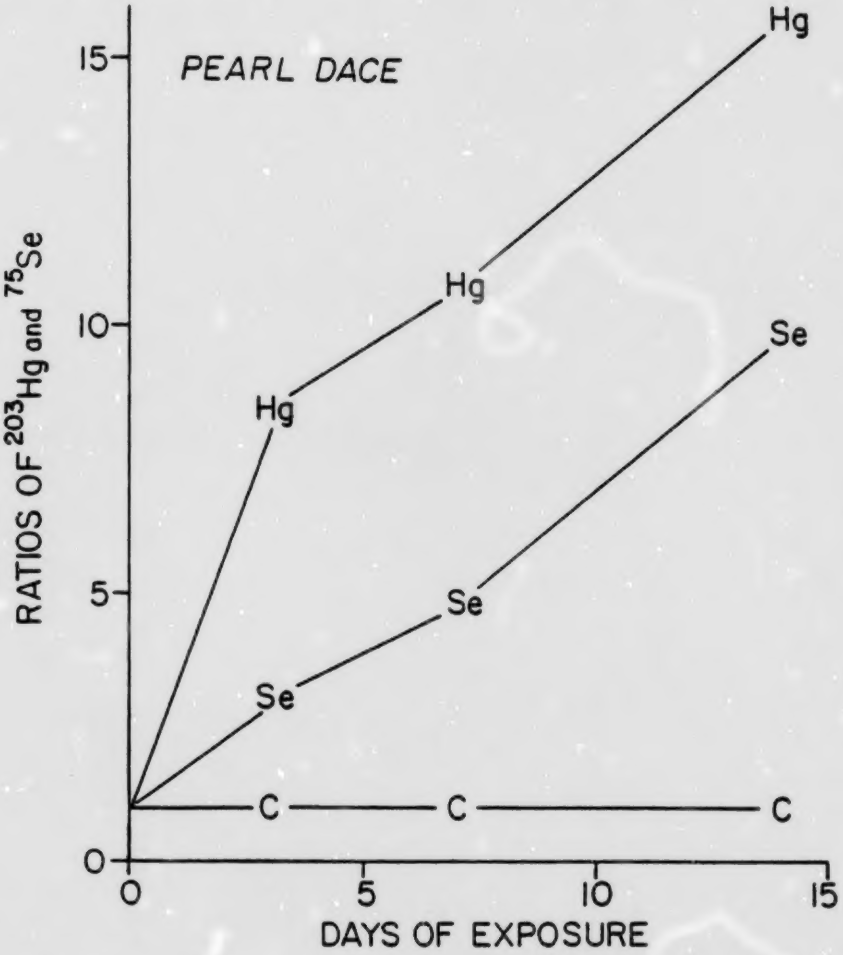

Fig. 1. Inhibition of pearl dace 203-mercury (Hg) and 75-selenium (Se) bioaccumulation by natural lake sediments. The data are expressed as ratios of ^{203}Hg and ^{75}Se activities of fish in an enclosure with a plastic bottom divided by fish activities in an enclosure with natural lake sediments (C).

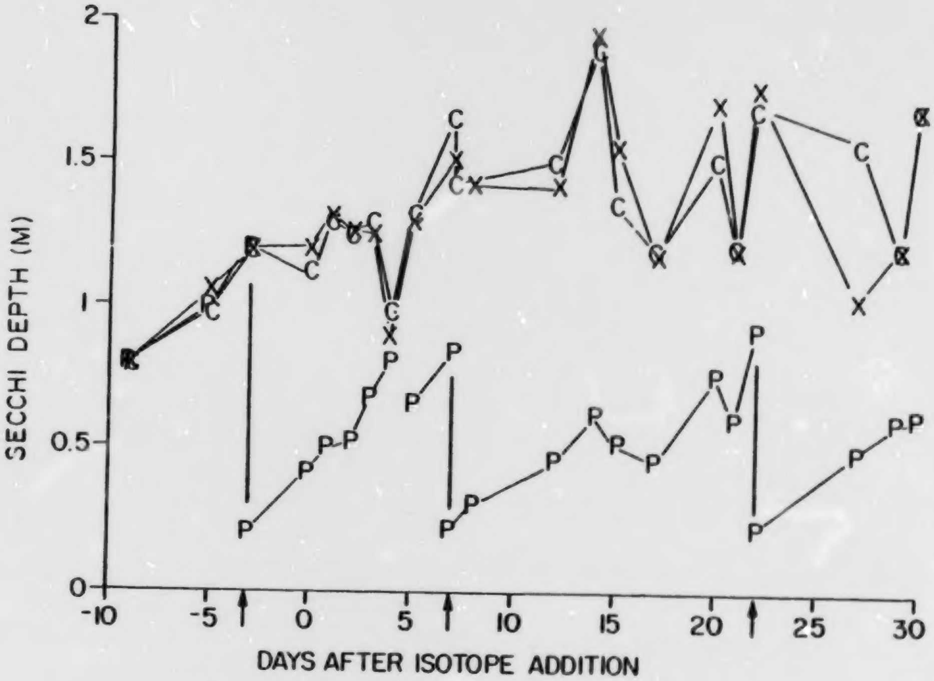

Fig. 2. Secchi depth readings in the controls (C and X) and the suspended sediment enclosure (P). Vertical arrows on the x axis indicate additions of sediment to the suspended sediment enclosure.

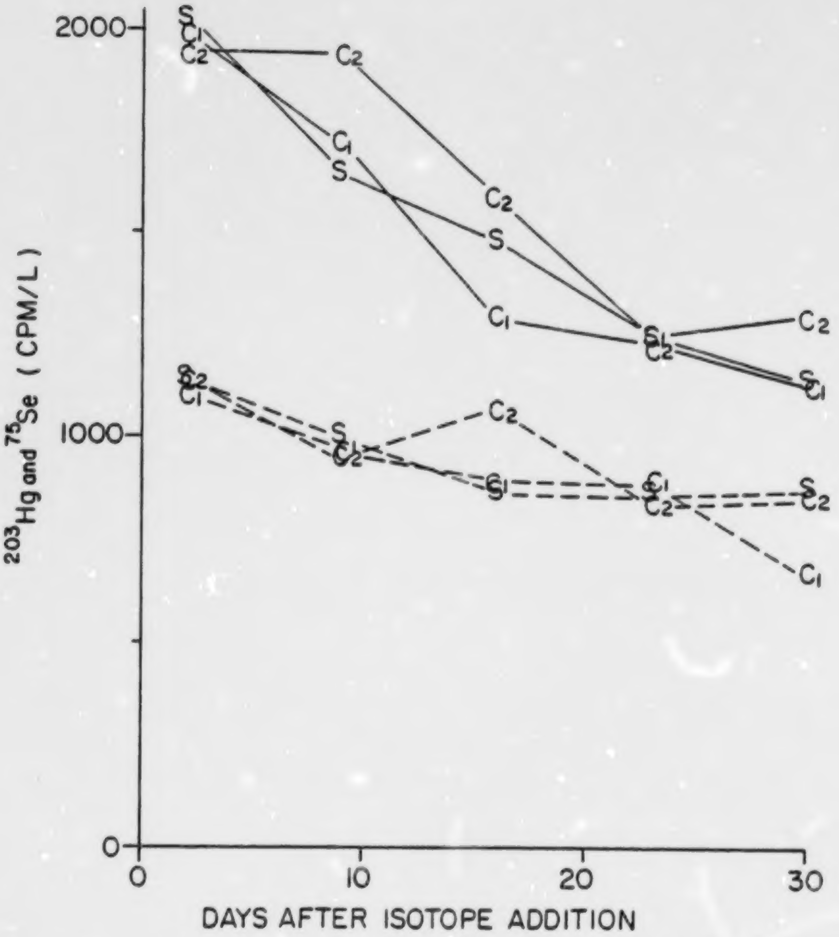

Fig. 3. Total concentration of ^{203}Hg (solid lines) and ^{75}Se (broken lines) in water samples from the control enclosures (C1 and C2) and suspended sediment enclosure (S) as a function of time. Isotope activities are sums of all mercury and selenium species.

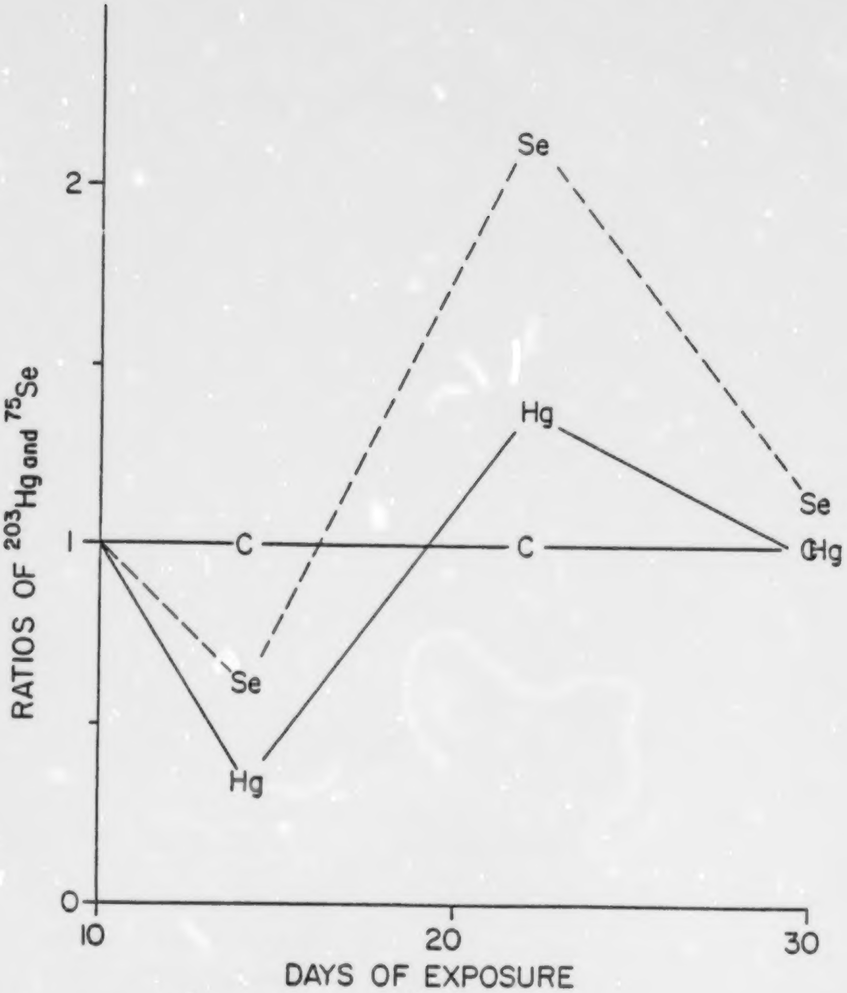

Fig. 4. Inhibition of haptobenthic 203-mercury (Hg) and 75-selenium (Se) bioaccumulation by addition of inorganic rich sediment to an enclosure. The data are expressed as ratios of ^{203}Hg and ^{75}Se activities of haptobenthos in the suspended sediment enclosure divided by activities of the haptobenthos in the combined control enclosures (C).

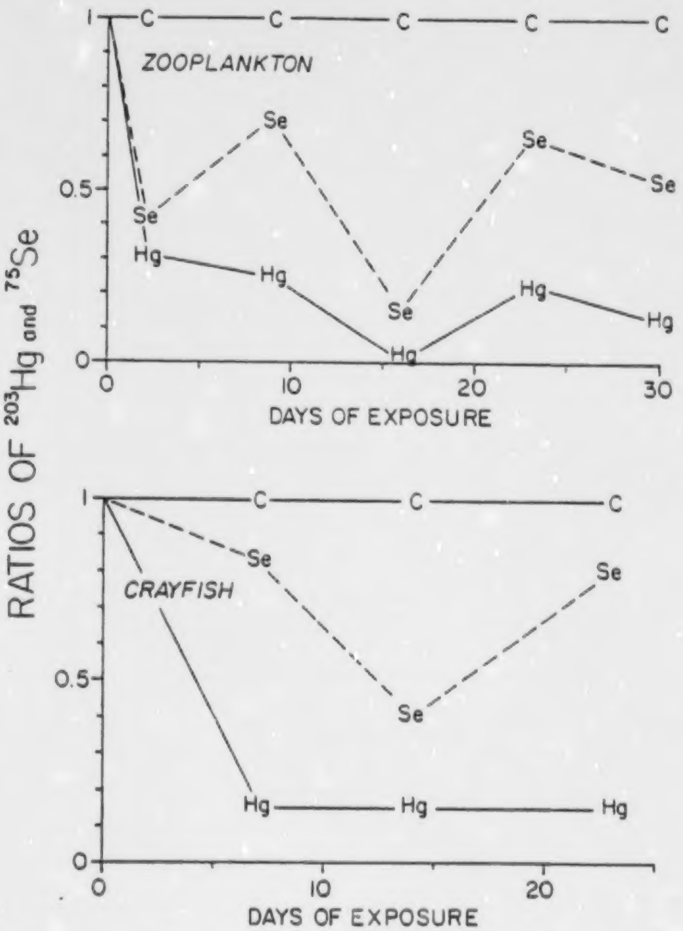

Fig. 5. Inhibition of zooplankton (upper panel) and crayfish (lower panel), 203-mercury (Hg) and 75-selenium (Se) bioaccumulation by addition of inorganic rich sediment to an enclosure. The data are expressed as ratios of ^{203}Hg and ^{75}Se activities in the suspended sediment enclosure divided by activities in the combined control enclosures (C).

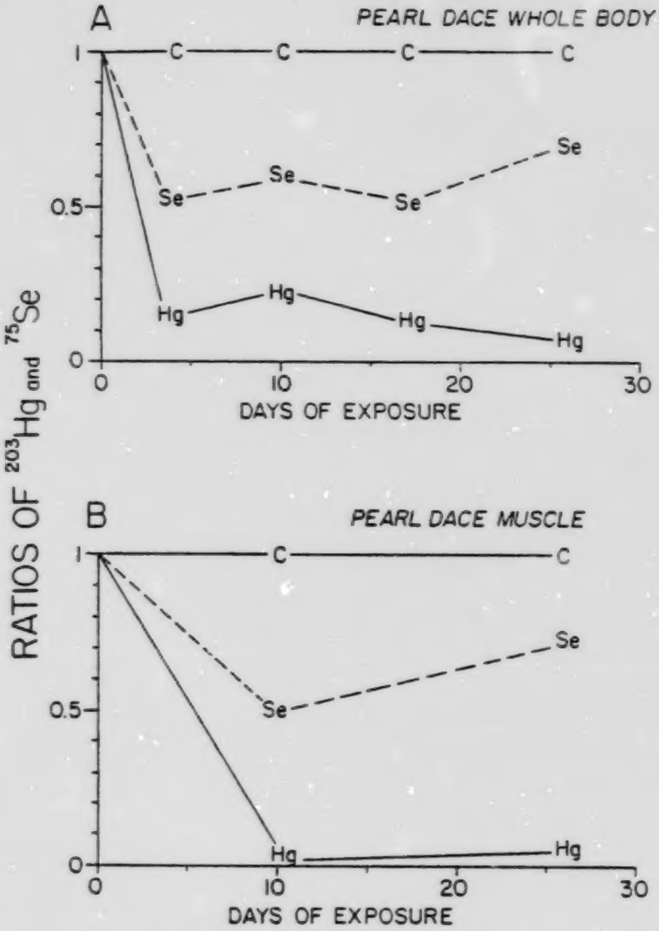

Fig. 6. Inhibition of 203-mercury (Hg) and 75-selenium (Se) bioaccumulation in pearl dace wholebody (upper panel) and muscle samples (lower panel) by addition of inorganic rich sediment to an enclosure. The data are expressed as ratios of ^{203}Hg and ^{75}Se activities in the suspended sediment enclosure divided by activities in the combined control enclosures (C).

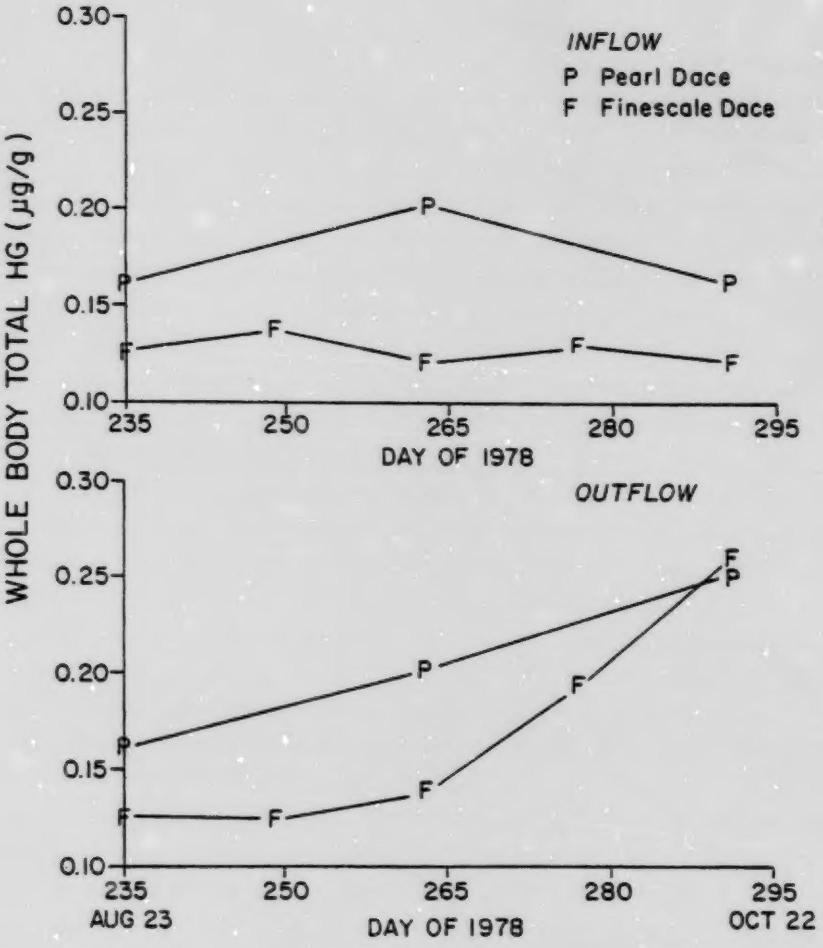

Fig. 7. Total mercury concentrations of finescale and pearl dace caged at the inflow (upper panel) and outflow (lower panel) of Clay Lake during the late summer and fall of 1978.

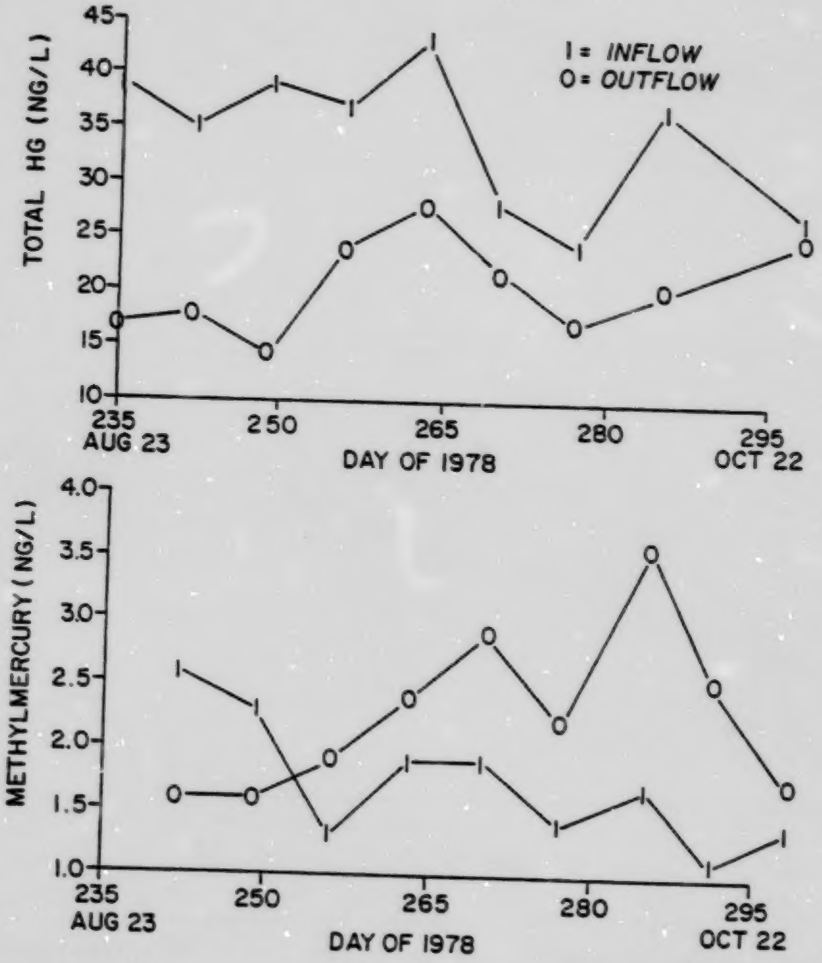

Fig. 8. Inflow and outflow concentrations of total (upper panel) and methyl mercury (lower panel) during the late summer and fall of 1978.

3. SELENIUM IN AQUATIC ECOSYSTEMS: ITS BIOGEOCHEMISTRY AND EXPERIMENTAL USE AS A MERCURY AMELIORATING AGENT

M. A. Turner and J. W. M. Rudd

INTRODUCTION

Point-source mercury pollution has been recognized as a severe environmental problem (National Academy of Sciences 1978; National Research Council 1979). For instance, Clay Lake (50°03'N, 93°30'W), which is the site for this study, is the first large reservoir on the Wabigoon River downstream of the pulp and paper mill at Dryden, northwestern Ontario. As a consequence of discharges of mercury from the mill, biota in this river-lake system exhibit extremely high burdens of mercury (Armstrong and Hamilton 1973, Parks et al. 1980). Also, mercury present in emissions from fossil fuel combustion (Klein et al. 1975) can be transported into the aquasphere (Gutenmann et al. 1976; Huckabee and Blaylock 1974) and be of public concern. Acidification of lakes may also mobilize mercury from watersheds and sediments to aggravate the problem. A combination of these processes could possibly explain suspected increases of fish mercury concentrations apparent during the early stages of lake acidification (Jernelov et al. 1976; Brouzes et al. 1977).

Selenium is an essential trace element with chemical properties similar to sulfur (Frost and Lish 1975; Vokal-Borek 1979). Selenium can be toxic in excessive amounts, and is not permitted in drinking water in Canada at concentrations above 10 μg Se/L (DeMayo et al. 1979; National Health and Welfare 1978). Selenium can reduce the toxicity of several heavy metals (Ag^+, Cd^{2+}, Hg^{2+} and As; reviewed by Vokal-Borek 1979) and, relevantly to our studies, reduce the severity of inorganic and methyl mercury poisoning in consumers of contaminated food (Chang et al. 1977; National Academy of Sciences 1978). Selenium has also been shown to reduce accumulation of mercury in pearl dace and crayfish; moreover, these animals bioaccumulated selenium efficiently at both trace (<0.2 μg Se/L) and increased (~100 μg Se/L) concentrations (Rudd et al. 1980a). Therefore, there is a possibility that careful use of selenium might alleviate mercury pollution problems both by reducing mercury concentrations in fish and by rendering the remaining mercury less toxic to fish consumers.

Selenium is also found in fossil fuel emissions (Hashimoto et al. 1970). It has been estimated that anthropogenic loading of selenium into the atmosphere in the United States is about ten times that of mercury on an atomic basis (Klein et al. 1975). Although the distance selenium is transported within the atmosphere may be short (Fingleton and Robbins 1980), selenium appears to be scavenged by rainfall in a manner similar to particulate trace metals (Hicks 1979).

The purpose of this experiment was to corroborate the observations of Rudd et al. (1980a) and to extend the investigation to lower selenium concentrations. If selenium proves to be an effective mercury ameliorating agent at environmentally acceptable concentrations, judicious additions of selenium could assist in alleviating the effects of point-source mercury contamination. In addition, it is quite possible that atmospheric fallout of selenium may reduce the severity of heavy metal pollution problems originating from combustion of fossil fuels.

METHODS

In general the methodology used in this experiment is similar to that described in Rudd et al. (1980a). Over the period of one day, polyethylene-walled experimental enclosures (surface and sediment area ~79 m^2, wall area ~52 m^2, volume ~130 m^3) were sealed into the clay sediments of a sheltered bay in the eastern basin of Clay Lake. The general experimental design consisted of five enclosures: two controls and one enclosure each at initial concentrations of 1, 10 and 100 µg Se/L. Each enclosure received separate additions of 5 mCi $^{203}Hg(NO_3)_2$ and 3 mCi $H_2{}^{75}SeO_3$ (1 Ci = 37 G Bq; New England Nuclear Corp.) on July 15, 1979. Approximately 15 ng/L inorganic mercury was added as carrier with the ^{203}Hg.

Water chemistry samples were taken at 0, 3 and 6 weeks. No consistent differences were observed among the enclosures in suspended or dissolved carbon, nitrogen and phosphorous species analyzed according to the methods of Stainton et al. (1977). Total and methyl mercury concentrations (~25 and ~1.5 ng Hg/L respectively) were also determined (Furutani and Rudd 1980), but were not different among the enclosures. Selenium concentrations in Clay Lake were below the analytical detection limit of 0.2 µg total Se/L.

Radioisotope rather than stable element additions were preferred for several reasons. The analytical sensitivity of radioisotope methods minimized the chemical additions required, eliminating inadvertent perturbation of the experimental ecosystems. Comparison of radioisotope activities between control and treatment conditions permitted us to determine the existence of a treatment effect. The high variability of stable selenium and mercury concentrations of the test organisms would have precluded discerning any but the largest of treatment effects. Further, addition of radioisotopes provided a definite time zero beyond which test and control conditions could be compared. Over the time course of this experiment, however, it is unlikely that the radioisotopes would have come into equilibrium with the stable elements within the experimental ecosystems. The addition of a radioisotope permitted us to "break into" the biogeochemical cycle of the corresponding element and to measure the effect of the experimental treatment upon movement of the element through its cycle. Because ^{75}Se was added in trace quantity with the sodium selenite added to the 1, 10 and 100 µg Se/L enclosures, its activity in biota of these enclosures can be used to calculate rates of accumulation of the stable selenium added.

Mercury and selenium isotopes were assayed using gamma spectroscopy techniques as described in Hesslein et al. (1980) and Rudd et al. (1980a). The 136 and 280 KeV peaks were used for ^{75}Se and ^{203}Hg, respectively. The contribution of ^{75}Se to the 280 KeV peak was corrected appropriately. All samples were decay corrected to the day of isotope addition. No correction was made for differences in sample geometry, although these are anticipated to have been small (<10%, Hesslein pers. comm.).

Water, haptobenthic and sediment core samples were usually taken, processed and analyzed as described previously by Rudd et al. (1980a), except that: anion and cation resins were combined to yield a mixed ion exchange column (Hesslein et al. 1980); strips of tube material, subsectioned into 25 cm strips (0-1.50 m), were suspended in each tube just after tube emplacement to quantify haptobenthic[1] colonization of the enclosure walls; duplicate cores, sectioned at 1 cm intervals to a maxiumum depth of 5 cm, were analyzed on each sampling occasion. Most biological samples collected for radioassay were frozen immediately upon collection using dry ice, and maintained in a frozen condition until radioassay. After radioassay, the polyethylene strips were dried and then scraped. the particulate material collected was weighed to quantify the areal amount of haptobenthos.

Carbon-14 incubator assays of phytoplankton primary productivity were performed biweekly (Fee 1973; Shearer 1976a, 1976b). Chlorophyll-a (Stainton et al. 1977) and phytoplankton samples were taken weekly. Phytoplankton samples were preserved with 2 mL of 40% formalin added within four hours of collection, and one mL of acid Lugol solution added two weeks later.

Weekly 60-liter zooplankton samples were taken using a modified Pennak tube (Salki 1981) in which collected water was passed through a 73 micron mesh net. Samples were preserved in the field by successive additions of 5 mL of ethanol and formalin. Radioassay samples were filtered through preweighed filters and dried at 60°C.

Adult crayfish (Orconectes virilis), collected from a nearby uncontaminated system, were put in the enclosures just prior to isotope addition. They were held in individual epoxy-coated cages upon the sediment and fed weekly with an excess of low mercury-containing flesh from young white suckers (~0.2 μg Hg/g wet weight).

Clams (Anadonta sp.), approximately 100 g each, were obtained from Clay Lake and held within cages placed on the enclosure sediments. Usually three clams were retrieved from each enclosure after 2, 4 and 7 weeks of exposure. Portions of the foot muscle were assayed for ^{203}Hg and ^{75}Se concentration.

Snails (~2 g) were collected from Clay Lake and two dozen added to each enclosure one week after isotope addition. Whole bodies, excluding the shells, were assayed for isotope concentration after one and two weeks of exposure.

One day after isotope addition, 70 adult pearl dace, Semotilus margarita (5.0 ± 0.7 g, mean ± SD, n = 38), obtained from a nearby uncontaminated lake, were added to each of the tubes (Table 1). To obtain estimates of whole body isotope concentrations, at least six pearl dace were sampled weekly using baited minnow traps tended hourly. Every second week, skeletal muscle samples were obtained from four dace selected randomly from each collection.

In addition to young of the year perch trapped during emplacement of the enclosures, thirteen were added intentionally to each tube three days after isotope addition (Table 1). Three perch were sampled every second week for whole body analysis. At the end of the experiment in mid-September, rotenone (~8 mg/L) was added to each of the enclosures. Fish were collected upon surfacing and frozen immediately.

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[1] "Haptobenthos" is the community associated with solid substrates (Hutchinson 1975). The term haptobenthos is preferred to "periphyton" because it emphasizes that the community is comprised of several classes of organisms; whereas the latter term is frequently used to describe only benthic algae.

The relationship between methyl and total mercury in muscle samples was assayed using a combination of gamma and scintillation counting techniques. Samples were originally counted using gamma spectroscopy and then extracted for radiolabelled methyl mercury according to the technique of Uthe et al. (1972) except that the last stage required to purify the sample prior to injection into a gas chromatograph was not performed. The 8 mL of toluene phase recovered from the extraction was added to 12 mL of PCS (Amersham/Searle) and counted using a Packard liquid scintillation counter. External standards were used to compare techniques.

RESULTS

Mercury and Selenium Geochemistry

With the exception of the 100 µg Se/L enclosure, ^{203}Hg activities in water were similar among all enclosures. After six weeks, ^{203}Hg activities were one-third of initial values (Fig. 1a). Fits of loss of ^{203}Hg from the water column followed first order kinetics equation ($0.966 \leq r^2 \leq 0.991$, n = 7; Table 2). Calculated half-times ranged from 20.3 to 22.7 days; but at 100 µg Se/L, a half-time of 14.0 days was observed (Table 2). This was corroborated by observation of the complementary increases in sediments (Fig. 1c).

Elevated selenium concentrations did not detectably alter partitioning of ^{203}Hg among particulate, ionic and undefined fractions (Table 4). However, the overall mean proportion of ^{203}Hg in the activated charcoal fraction appears to have been lowered from 30% ± 0% (SE) in the controls to 23% ± 1% (SE) at elevated selenium concentrations.

In the control situation, with background concentrations of selenium (<0.2 µg Se/L), ^{75}Se activity in water stabilized within four weeks at about one-half the initial value (Fig. 1b). In contrast, at elevated levels, selenium concentrations in water decreased almost linearly with time and did not stabilize within six weeks. This difference in pattern of movement appeared to be corroborated by observed sediment concentrations (Fig. 1d). Half-times of selenium in water may have increased from 47 to 58 days with increasing concentration of selenium.

There was a shift of ^{75}Se from the charcoal to ionic fraction (Table 4) which increased significantly ($P<0.05$) with increasing concentration of selenium. Earlier observations indicate that ionic selenium exists predominantly as anion (Rudd et al. 1980a). In the control tubes, the fraction on particulate decreased rapidly with time, decreasing from 49% on day 2 to 13% on day 9 (not shown). In contrast, the fraction on particulate in the elevated selenium tubes was always observed to be very low, usually less than 2% (Table 4).

Haptobenthic areal activities of ^{203}Hg increased until the fourth week of exposure (Fig. 1e). After two weeks, rate of bioaccumulation of ^{203}Hg per unit mass decreased with time paralleling water concentrations (not shown). This probably reflects the interaction of increasing haptobenthic biomass (not shown) with decreasing activity of isotope in water (Fig. 1a).

Elevated selenium levels did not influence haptobenthic accumulation of ^{203}Hg (Fig. 1e) in contradiction to Rudd et al. (1980a). However, in Rudd et al. (1980a) the response of an established community was observed; whereas the more recent observation is that of a newly developing community.

Areal bioaccumulation of ^{75}Se by the wall haptobenthos was inversely proportional to stable selenium concentration (Fig. 1f). In the 10 and 100 µg Se/L enclosures, ^{75}Se activity per unit dry weight of haptobenthos (not shown) declined after two weeks of exposure. Selenium concentration continued to increase throughout the experiment in the 1 µg Se/L enclosure. Maximum observed selenium concentrations were 16, 114 and 1460 µg/g (dry weight) in the 1, 10 and 100 µg Se/L enclosures, respectively.

For these experiments, initiated without established wall haptobenthos, the major geochemical sink for both isotopes was the sediment. One-half and two-thirds of the ^{75}Se and ^{203}Hg, respectively, were present in the sediments after six weeks; while less than two percent of either isotope was found in the haptobenthos.

Selenium Bioaccumulation and Toxicity

Algal ^{14}C primary productivity was stimulated by 100 µg Se/L, but was not substantially altered by 1 or 10 µg Se/L (Fig. 2a). Chlorophyll-a concentrations seemed to reflect the photosynthetic response; a large increase at 100 µg Se/L, but essentially no difference among the remaining enclosures (Fig. 2b).

Algal species composition seems to have changed in response to higher selenium concentrations. All enclosures were initially dominated by chrysophytes, shifting with time in both controls to relatively equal representation of chlorophytes and chryptophytes. Algal groups dominating the selenium enclosures at the end of the experiment were chlorophytes (*Volvox aureus*) at 1 µg Se/L, chrysophytes (*Dinobryon divergens*) at 10 µg Se/L and cyanophytes (*Aphanizomenon flos-aquae*)at 100 µg Se/L. The bloom of *A. flos-aquae* resembled that observed concurrently in the eastern basin of Clay Lake. Overall phytoplankton species composition was most similar to the controls at 1 µg Se/L.

Zooplankton ^{75}Se activities (Fig. 3a) rose rapidly and then declined, approximately following water activities (Fig. 1b), in both controls and to a lesser extent at 1 µg Se/L. A temporal pattern at 10 and 100 µg Se/L was not apparent (Fig. 3a). Selenium-75 in crayfish (Fig. 3b), snails and clams (not shown) increased or stabilized eventually with time. This may be a consequence of more rapid turnover in zooplankton populations, and/or water rather than food predominating as a vector for Se uptake by the zooplankton.

Concentration of selenium within all invertebrates was proportional to ambient selenium concentration (e.g., Fig. 3b). At 100 µg Se/L, all invertebrates appeared to achieve stable concentrations: crayfish whole bodies (0.8 µg Se/g, wet weight), snail whole bodies(4.0 µg Se/g) and clam foot muscle (1.2 µg Se/g). In the 1 µg Se/L enclosure, Se concentrations in crayfish continued to increase rapidly after six weeks; but at 10 µg Se/L, a less rapid increase was observed (Fig. 3b).

Whole body selenium concentrations in fish increased throughout the experiment and in proportion to the ambient selenium concentration (Fig. 4). Concentrations increased consistently according to the following species sequence: adult pearl dace < young of the year yellow perch < young white sucker (Fig. 4).

The concentration of selenium in skeletal muscle of pearl dace, relative to their whole body, was dependent upon both the ambient level of selenium and the duration of exposure. After eight weeks, the ratio of concentrations of muscle: whole-body in dace of the two controls was 37% ± 1% (SE of the two means, each comprising four individuals). Corresponding percentages at 1, 10 and 100 μg Se/L were 46%, 63% and 77%, respectively.

No fish mortalities were observed that could be attributed to increasing selenium concentrations. Growth rates of yellow perch were greatest at 100 μg Se/L, and were not appreciably different among the other enclosures. The mean fork length of yellow perch at 100 μg Se/L at the end of the experiment was 71.8 ± 0.8 mm (±SD, n = 5) versus 60.0 ± 2.1 mm (SE) in the other four enclosures. This growth enhancement may be due to the elevated photosynthetic rates (Fig. 2a) rather than to a direct effect of selenium.

Mercury Bioaccumulation

The relationship between methyl and total ^{203}Hg in skeletal muscle of pearl dace is a sigmoidal function of time (Fig. 5a). Initially the proportion of methyl to total ^{203}Hg was low, but between four and six weeks of exposure, there was a rapid increase.

After eight weeks, the proportion of labelled methyl to total ^{203}Hg was 75%, 85% and 100% in pearl dace, yellow perch and white suckers of a control enclosure, respectively (Fig. 5b). In contrast, crayfish had only 25% methyl after six weeks of exposure.

Mercury-203 activities in undifferentiated zooplankton samples, snail whole bodies and clam foot muscle were not affected during their exposure periods (not shown). In contrast, ^{203}Hg activities in crayfish whole bodies (Fig. 6a) and abdominal muscle (Fig. 6b) were reduced at 10 and 100 μg Se/L, but not at 1 μg Se/L.

Although selenium did not influence the final proportion of methyl:total ^{203}Hg in skeletal muscle of pearl dace (Fig. 5c), all fish species exhibited a concentration-dependent reduction in ^{203}Hg activity due to selenium. Final activities of total ^{203}Hg in whole bodies of pearl dace (Fig. 7a) and skeletal muscle (Fig. 7b) were reduced at 10 and 100 μg Se/L, but not at 1 μg Se/L. Yellow perch had lower ^{203}Hg activities at 10 and 100 μg Se/L (Fig. 7c); and at 1 μg Se/L, body burdens of ^{203}Hg were consistently lower (68% ± 3.4%, ±SE, n = 4 exposure periods) than in the controls. Similarly, young white suckers, which exhibited the highest concentrations of selenium in whole bodies at 1 μg Se/L (Fig. 4), also showed a significant reduction in whole body ^{203}Hg at 1 μg Se/L (Fig. 7d).

DISCUSSION

Geochemistry

The interrelationship of mercury and selenium in the water column was dependent upon the concentration of selenium. At 100 μg Se/L the rate of movement of mercury to the sediments was enhanced (Fig. 1a; Table 2) confirming previously presented data (Rudd et al. 1980a). Although there was no such effect apparent at 1 and 10 μg Se/L (Fig. 1a; Table 2), the chemical form of ^{203}Hg was affected with the amount associated with the activated charcoal fraction (dissolved organics) being reduced (Table 4).

At natural selenium concentrations, i.e. in the control enclosures (<0.2 µg Se/L), ^{75}Se activity in water appeared to stabilize after only 4 weeks at one-half of initial activities (Fig. 1b). In the controls, selenium dynamics were dominated by the charcoal fraction (nonpolar dissolved organics, NDO; Fig. 2b). Selenium is strongly attached to this fraction because addition of 1 mg Se/L of stable selenium failed to dislodge ^{75}Se that had been bound previously by the NDO when added at trace selenium concentrations (Rudd et al. 1979). The strength of this binding to NDO is consistent with the observation of Jackson et al. (1980) that selenium is bound strongly to humic matter.

In the controls, after two weeks, the initially large proportion of ^{75}Se on particulates (≈50%) had either settled out or been redistributed among the other fractions. Subsequent stabilization of NDO-dominated selenium (Table 4) between water and sediments (Fig. 1b) suggests that NDO-selenium has a different removal rate than either the particulate or ionic fractions.

As in Rudd et al. (1980a), elevated selenium concentrations resulted in ionic selenium predominating (Table 2), probably as the anion. There was less NDO-selenium with increasing concentration of stable selenium (Table 4), declining from 27% to 19% at 1 and 100 µg Se/L, respectively. This suggests that the NDO fraction was largely saturated at 1 µg Se/L because a much larger proportion (63% ± 1%, SE) of ^{75}Se was associated with the NDO fraction in the control enclosures (Table 4).

Stable partitioning of ^{75}Se between water and sediments was not apparent after six weeks in all selenium enclosures (Fig. 1; Table 3). Although initial movement of selenium to the sediments was not as rapid at elevated selenium concentrations as in the controls (Fig. 1b), a greater proportion, being ionic (Table 4), would be available to move to the sediments in the long term. Observations of either longer duration or increased sediment to water ratio are required to determine the final water concentrations resulting from these levels of selenium additions.

As before (Rudd et al. 1980a), when enclosures with established haptobenthos were used, the major geochemical sink for both mercury and selenium was in sediment (Fig. 1c vs. 1d and 1e vs. 1f). However, proportionately less of the selenium, but not ^{203}Hg, resided in the haptobenthos with increasing concentration of selenium (Fig. 1f).

The movement of ^{75}Se to sediment was related to the level of addition. After six weeks, ^{75}Se was confined to the upper one cm stratum of sediments; but in the earlier experiment, a mixed layer of three cm had been observed (Rudd et al. 1979). Based upon an eventual mixing depth of 5 cm (Schindler et al. 1977), at the rate of accumulation observed (Fig. 1d), a one-year continued addition of 1 µg Se/L would increase sediment selenium by 0.08 µg/g (dry weight), versus current levels of 0.4 µg/g (Rudd et al. 1980a). In contrast in only six weeks, at 100 µg Se/L, sediment selenium was increased almost 10-fold in the upper one cm. Additionally, a noticeable odor was detected in the sediments of the 100 µg Se/L enclosure, possibly due to an organically reduced selenide (Chau et al. 1976).

Bioaccumulation of Selenium

Selenium is bioaccumulated by all components of aquatic foodwebs tested (Adams and Johnson 1977; Fowler and Benayoun 1976a, 1976b; Huckabee and Blaylock 1974; Rudd et al. 1979, 1980a;Sandholm et al. 1973). Although the selenium requirements of mammals have been intensively studied (reviewed by Vokal-Borek 1979), there are few investigations of the requirements of individual aquatic organisms.

Selenium may be essential to aquatic foodwebs. Lindstrom and Rhode (1978) demonstrated that the dinoflagellate *Peridinium cinctum* could grow only in culture media containing selenium and that in lake water productivity was stimulated by their highest addition of 0.16 μg Se/L. In the current experiment, growth of mixed algal populations was stimulated at 100 μg Se/L (Fig. 2). Water concentrations of 0.4 ± 0.2 μg Se/L plus 0.07 μg Se/g and 0.4 IU Vitamin E/g of dry diet were found to be sufficient to prevent selenium deficiency in laboratory-reared rainbow trout (*Salmo gairdneri*; Hilton et al. 1980). Dietary levels between 0.15 and 0.38 μg/g (dry weight) were found to be optimal, although a ten-fold higher concentration was toxic (Hilton et al. 1980).

Available information indicates that the food vector increases in importance at higher levels in the food web. The green alga, *Scenedesmus dimorphus*, accumulated selenium directly from water, but the rate was a property of chemical form (Sandholm et al. 1973). *Daphnia* sp. accumulated selenite and selenomethionine directly from water, but were additionally able to assimilate selenium by ingestion of algae (Sandholm et al. 1973). In marine mussels and shrimp, the relative distribution of ^{75}Se among organs was more similar to the distribution of stable selenium when incorporated from food rather than from water directly (Fowler and Benayoun 1976a, 1976b). Although several species of fish can accumulate selenium from water directly (Hodson et al. 1980; Sandholm et al. 1973; sections 4 and 8) at trace concentrations (<0.2 μg Se/L) assimilation from food predominates (Rudd et al. 1980a, section 4), but uptake from water appears equally important at 10 μg/L (section 4). This latter observation may partly be due to suppression of dietary assimilation of selenium in the presence of elevated water concentrations (section 4).

The size or life-history stage of an organism is important in determining responses to an alteration in ambient selenium concentration. This is shown by the greater sensitivity of fry to toxic selenium concentrations compared with adult life-history stages (Cardwell et al. 1976; Schultz et al. 1980). This may partially explain the more rapid accumulation of selenium by young of the year perch and juvenile white suckers relative to adult pearl dace found in this work (Fig. 4). This is consistent with the observation that young fish bioaccumulate mercury more rapidly than do older fish (reviewed by Armstrong 1979 and Huckabee et al. 1979). Within the food web, responsiveness, and potential variability among individuals within a population, can be expected to be inversely proportional to body turnover time of selenium, and approximately proportional to lifetime of the organism. Rapidity of change in body burden in response to fluctuations in ambient selenium should be greatest for algae, intermediate for zooplankton and zoobenthos, and least for large fish species. Algae, and to a lesser extent herbivorous zooplankton, will tend to reflect prevailing water concentrations (Fig. 3a); whereas, longer-lived organisms will be more affected by foodweb concentrations - partially sediment determined (section 4).

Although selenium concentrations vary among fish species at a given location (Fig. 4, Beal 1974, Adams and Johnson 1977), variability is greater among waterbodies. Regional mean concentrations in fish within Central Canada, as reported by Beal (1974), ranged from 0.13 µg/g (wet weight) in Alberta to 0.5 µg/g in the Great Lakes. The reported range of concentrations in fish is from 0.1 µg/g for Lake Ontario catfish (Beal 1974) to 1.5 µg/g found in whitefish and sheepshead taken from Lakes Huron and Erie (Beal 1974, Adams and Johnson 1977). At the Experimental Lakes Araa near Clay Lake, the overall species mean was found to be 0.50 ± 0.13 (±SD, n = 14, 3sp; Turner and Rudd, unpublished data). Therefore, the Clay Lake species mean of 0.14 ± 0.03 (n = 65, 5 sp; Turner and Rudd, unpublished data) in skeletal muscle is particularly low.

Within a particular fish population, selenium concentrations are variable. As for mercury (Scott and Armstrong 1972), selenium can correlate with fish size in some species (Turner and Rudd, unpublished data); although fish age may be a better independent variable (Scott 1974). This may be the result of input exceeding turnover rate, or inclusion of a selenium fraction which does not "turn over", or does so at a much slower rate. Selenium atoms bound to mercury could be such a fraction. Interestingly, the correlation between selenium and mercury concentrations (not shown) was always observed to be better than corresponding correlations between selenium and length.

Concentrations of selenium vary among tissues of individual fish (Hodson et al. 1980; section 4 and 8). Highest concentrations are observed in the liver (section 4) and kidney, both of which are postulated to be involved with selenium regulation and excretion (Hodson et al. 1980), and possibly mercury demethylation (Burrows and Krenkel 1973). The ratio of selenium in muscle to that in the whole body of pearl dace correlated with the level of ambient selenium, ranging from 37% in the controls to 77% at 100 µg Se/L.

Aquatic Toxicity of Selenium

Water quality criteria include two pertinent guidelines: 10 µg Se/L for drinking water (National Health and Welfare 1978); and 50 µg Se/L in water used for recreational purposes (DeMayo et al. 1979). In our experiments there were some changes in the phytoplankton community. The effect at 1 µg Se/L was equivocal, but at both 10 and 100 µg Se/L, algal species composition was altered. Given the substantially increased algal productivity (Fig. 2) and fish growth subsequently observed at 100 µg Se/L, the change may not be harmful to the ecosystem.

Information contained in the summary of aquatic literature (Table 5) suggests that 10 µg Se/L and below will probably not present a hazard to the aquatic organisms listed, although further and more sensitive tests are required for verification (section 8). At 50 µg/L however, there could be problems with some zooplankton (Schultz et al. 1980), and physiological changes in fish after long term exposures (Hodson et al. 1980).

Toxicity thresholds are probably dependent upon rates of selenium bioaccumulation. Chemical species most easily bioaccumulated may be most toxic, with selenite species more toxic than corresponding selenate ions (Niimi and LaHam 1975). When accumulated from the food web in addition to direct uptake from water, ambient concentrations required to induce a toxic response will be lower. Life history stages demonstrating rapid uptake will be more sensitive; e.g. juveniles appear to accumulate Se more rapidly than adults and exhibit correspondingly lower toxic threshold concentrations (Browne and Dumont 1979; Cardwell et al. 1976; Schultz et al. 1980).

Water quality characterisitics altering bioaccumulation should also modify toxicity. For example, added clay reduced uptake of ^{75}Se (section 2); and therefore, would be expected to reduce toxicity.

Influence of Selenium Upon Mercury Bioaccumulation

The observation that 100 μg/L selenium reduced bioaccumulation of mercury in pearl dace and crayfish (Rudd et al. 1980a) was confirmed and extended to include yellow perch and white sucker (Fig 7). A smaller reduction in mercury bioaccumulation by these fish species was observed at 10 μg Se/L (Fig. 7). At 1 μg Se/L only young white suckers, which accumulated selenium to the greatest extent (Fig. 4), showed a significant reduction in ^{203}Hg activity (Fig. 7); although body burdens of ^{203}Hg in yellow perch were lower at 1 μg Se/L than in the controls. At all levels of added selenium, whole body concentrations of selenium increased consistently from dace to perch to sucker (Fig. 4). Thus, the extent to which bioaccumulation of ^{203}Hg decreases in response to selenium treatment, appears proportional to the amount of selenium bioaccumulated by that fish.

Reduction in bioaccumulation of ^{203}Hg has also been found in predaceous megalopterans and chaoborids in related observations (B. Townsend pers. comm.). Reductions were not seen in detrivorous insects (B. Townsend pers. comm.), clams, snails, and mixed zooplankton populations (not shown). The ability of selenium to reduce the bioaccumulation of mercury appears to depend on the position of the organism in the food web. At the lowest levels, there is little or no selenium effect, but at higher ones monitored in these enlosure ecosystems, a reduction in uptake of mercury was apparent. One would predict that predaceous fish would show a greater reduction in mercury bioaccumulation at low selenium concentrations than the detrivorous and omnivorous fish used in these experiments, and this is found to be so (section 4).

Selenium as an aquatic mercury ameliorating agent

Selenium is an essential element (reviewed in Vokal-Borek 1979) which can alleviate mercury poisoning in mammals (Chang et al. 1977), and can reduce bioaccumulation of mercury in aquatic foodwebs (Rudd et al. 1980a, Fig. 7 and 8; section 4). The use of selenium as an ameliorating agent should be approached cautiously, because in excess, selenium can be toxic to humans (Shapiro 1973) and to aquatic biota (Table 5; section 8). Selenium is active metabolically (Frost and Lish 1975; Shapiro 1973), and the window between optimum and excessive amounts may be correspondingly small (Hilton et al. 1980).

In terms of the dosage and feasibility of selenium addition, it is useful to consider the specific example of the Wabigoon River system. This system (Armstrong and Hamilton 1973; Parks et al. 1981) is an extreme example of mercury contamination in an inland water course. Unfortunately, selenium concentrations in aquatic biota are also particularly low (see previous discussion). Consequently, fish mercury:selenium ratios are the highest of which there is knowledge. The low selenium concentrations may be a consequence of low selenium loading to the system, though this is not known. The large quantities of sediment in suspension may also be an important determining factor (section 2), which together with the high productivity of the system, can act further to reduce fish selenium concentrations (section 5). In addition, it is possible that the heavy mercury burdens in fish have induced selenium deficiency as observed experimentally in pigs (Froseth et al. 1974).

It should be possible to increase fish selenium concentrations threefold in the Wabigoon system to around 0.5 μg/g and nearer to the more typical levels found presently at the Experimental Lakes Area (see previous discussion) and in the Great Lakes (Adams and Johnson 1977; Armstrong and Lutz 1977a and b; Beal 1974). In our experiments this level was approached in young of the year yellow perch and juvenile white suckers in the 1 μg Se/L enclosure (0.24 and 0.38 μg/g respectively, Fig. 5) after only two months of exposure. Thus, over the lifetime of a fish, it is possible that a water concentration of less than 1 μg Se/L would be required.

Although the single experimental addition of 1 μg Se/L did not always reduce the rate of ^{203}Hg bioaccumulation in non-predatory fish (Fig. 8), with the food web enhancement effect observed in section 4, mercury concentrations in predatory fish (fish species most often consumed by humans) may be reduced at 1 μg Se/L. At least there should be substantial improvement in the Hg:Se ratio, reducing the toxicity of mercury in fish at its present concentration. At best, there would also be a reduction in mercury concentration in all fish.

Selenium is accumulated efficiently through the food web (Rudd et al. 1980, section 4), so that it should not always be necessary to maintain selenium indefinitely at an elevated concentration in water. For example, it is possible that surface sediment concentrations rather than water concentrations, per se, control levels of selenium in fish. Further additions could be made as required in conjunction with close chemical monitoring as would befit such a scheme for other reasons.

Although it is probably neither the level nor the schedule of addition which would be used, with a continuous 1 μg Se/L treatment it can be demonstrated that there should be substantial safety margins for both humans and aquatic biota. One μg Se/L is one-tenth of the presently accepted drinking water maximum (Canadian Drinking Water Standards and Objectives 1978). Also, western Lake Erie concentrations are reported to be 10 to 40 times higher (Adams and Johnson 1977). Sublethal toxicity levels in humans would not be reached until a person persisted in consuming the unlikely quantity of 40 kg of 0.5 μg/g fish (wet weight) per day - calculated from data presented in De Mayo et al. (1979) assuming an assimilation efficiency of 100%. From this experiment, it seems that increased selenium may alter phytoplankton species composition. Otherwise, from the toxicity information currently known (summarized in Table 5), 1 μg Se/L is 50 times lower than known chronic sublethal concentrations for the most sensitive of aquatic biota tested, and is 10^3 times lower than the lethal limit of the most sensitive aquatic vertebrate tested. Moreover, fish at least, appear able to regulate selenium bioaccumulation (Hodson et al. 1980; section 4). A further safety feature is that downstream of Clay Lake, elevated concentrations would be substantially diluted at Ball Lake, the confluence of the Wabigoon and English River systems. Given that concentrations of mercury in biota at Ball Lake, and further downstream, are less than those characteristic of Clay Lake biota (Armstrong and Hamilton 1973, Parks et al. 1981), the availability of the additional selenium would be proportional to need.

Further research is warranted before a proper assessment can be made as to the risk:benefit of selenium as an aquatic ameliorating agent. We require additional information on the sublethal toxicity of selenite and its metabolites to individual organisms and eocsystems at anticipated concentrations under prevailing system conditions. More refined information is also needed about effective dosage and schedule of addition(s), particularly as they interact with other proposed amelioration strategies. Much of this information could be obtained using continuous culture techniques _in situ_ (e.g. DeNoyelles and O'Brien 1974), in combination with enclosure experiments. Subsequently, the proposed strategy could be tested with an experimental addition of selenium to a whole lake.

In summary, selenium continues to appear as a promising amelioration strategy in aquatic ecosystems characterized by elevated mercury and relatively low levels of selenium in biota. Selenium is bioaccumulated easily by aquatic food webs, favorably altering the mercury:selenium ratio of the biota. It may reduce fish mercury concentrations at selenium levels that are within acceptable limits, especially given the food web enhancement observed. In addition, such additions appear practicable. At this time, the risk cannot be assessed accurately because the minimum effective concentration and schedule of addition(s) remain to be determined. In the particular case of the Wabigoon River system, the biota are so severely contaminated that selenium addition in isolation would probably be insufficient. A more powerful amelioration strategy (section 1) would be to combine selenium addition with other techniques such as reduced anthropogenic loading of mercury, suspension of sediments, and size-selective fishing.

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Table 1. Initial densities of fish (kg/ha) in the experimental enclosures.

	Control		Selenium (g/L)		
	One	Two	1	10	100
Fish trapped at the time of enclosure emplacement[1]					
Yellow perch[2]	5.1	1.3	6.1	9.6	0.8
White sucker[3]	4.9	4.4	10.3	3.9	0.9
Experimental fish additions					
Yellow perch	1.5	1.5	1.5	1.5	1.5
Pearl dace	48	48	48	48	48

[1] Several young yellow perch and white suckers were trapped during installation of the enclosures. The numbers of each were determined from sampling and addition of rotenone to the enclosures at the end of the experiment.

[2] Yellow perch were estimated to initially weigh 1.0 g each.

[3] One-half of the sucker biomass observed in the final sample was assumed to result from growth during the experiment, approximately in parallel with observed rates of growth by perch.

Table 2. Description of the movement of ^{203}Hg out of the water columns of the enclosures using the first order kinetics equation: $C_t = C_o \times e^{(-\ln 2 \times \Delta t/t_{0.5})}$. C_t is the isotope activity at time Δt (days after addition), C_o is the initial activity, and the rate of change in activity is expressed as $\log_e/t_{0.5}$ with $t_{0.5}$ equal to the half-time of the isotope in the water column (Hesslein et al. 1980). N = 7 for each treatment condition.

		Control		Selenium		
Parameter	Units	One	Two	1	10	100
r^2		0.987	0.989	0.996	0.968	0.991
C_o	cpm/L	3400	3340	3550	3430	3660
$t_{0.5}$	days	20.8	22.7	20.7	20.3	14.0

Table 3. Description of the movement of ^{75}Se out of the enclosures' water columns using

$$(C_t - C_e) = (C_0 - C_e) \times e^{(-\ln 2 \times \Delta t/t_{0.5})}$$

for the controls, and the special case of $C_e = 0$, or

$$C_t = C_0 \times e^{(-\ln 2 \times \Delta t/t_{0.5})}$$

for the situation of added selenium. C_t, C_0 and $t_{0.5}$ are as described in Table 2. C_e is the equilibrium concentration of ^{75}Se in water (R. Hesslein pers. comm.). The more general model provided a better fit for the control enclosures ($r^2 > 0.95$) than did the simpler version ($r^2 = 0.88$). Half-times are not comparable directly between models, and therefore, between control and selenium conditions. N usually equals 7.

		Treatment				
		Controls		Selenium		
Parameter	Units	One	Two	1	10	100
r^2		0.974	0.953	0.946	0.944	0.980
C_0 (±SD)	cpm/L	2180 (±45)	2093 (±55)	2230	1840	2080
C_e (±SD)	cpm/L	1089 (±31)	984 (±33)	0	0	0
$t_{0.5}$ (±SD)	days	8.2 (±0.1)	7.6 (±1.0)	47	50	58

Table 4. Partitioning of ^{203}Hg and ^{75}Se in water into particulate, charcoal, ionic and undefined (^{203}Hg only) fractions. The percentage means of the time series (±SD, n = 7) are presented.

		Treatment				
		Controls (<0.2 μg Se/L)		Selenium (μg/L)		
Isotope	Fraction	1	2	1	2	3
^{203}Hg	Particulate (>0.45 μ)	29.5 (±15.1)	19.0 (±2.2)	19.4 (±4.3)	20.4 (±2.9)	26.1 (±8.3)
	Activated Charcoal	29.6 (±6.5)	29.9 (±9.0)	22.8 (±7.3)	24.2 (±3.3)	22.4 (±4.5)
	Ionic	13.4 (±3.8)	17.5 (±3.1)	18.8 (±7.8)	15.6 (±6.3)	18.8 (±4.4)
	Undefined	27.6 (±11.6)	33.6 (±9.5)	39.0 (±7.9)	39.8 (±10.2)	32.8 (±8.9)
^{75}Se	Particulate (>0.45 μ)	15.8 (±16.2)	14.4 (±15.9)	2.1 (±0.2)	1.5 (±0.5)	2.2 (±3.2)
	Activated Charcoal	59.4 (±12.2)	62.3 (±14.8)	27.3 (±7.1)	23.8 (±2.9)	18.8 (±3.4)
	Ionic	22.1 (±5.0)	23.4 (±8.0)	70.1 (±7.2)	74.7 (±3.1)	79.0 (±4.3)

Table 5. Summary of literature examining the toxicity of selenium to aquatic biota.

Organism	Selenium compound tested	Reference number*	Observations
Bacteria			
Escherichia coli	$SeO_3^=$	1	96-hr LC_{50}: 90 mg Se/L
Algae			
Scenedesmus	$SeO_3^=$	1	96-hr LC_{50}: 2.5 mg Se/L
Peridinium cinctum	$SeO_3^=$	7	Growth at 1.6 μg Se/L was 80% of the optimum rate observed at 50 mg Se/L in culture medium; but in lake water the optimum was greater than the observed 158 mg Se/L

Zooplankton			
Microregma	$SeO_3^=$	1	96-hr LC_{50}: 183 mg Se/L
Daphnia magna	$SeO_3^=$	5	Survival and reproduction unaffected at <0.43 mg Se/L
Daphnia pulex	$SeO_3^=$	12	96-hr LC_{50}: fed adult, 0.44-0.57 mg Se/L (95% confidence interval) 96-hr LC_{50}: unfed adult, 0.016-0.31 mg Se/L (95% confidence interval) 96-hr LC_{50}: fed juvenile, 0.12-0.14 mg Se/L (95% confidence interval) Toxicity increased with duration of exposure
Daphnia	$SeO_3^=$	1	48-hr LC_{50}: 2.5 mg Se/L
Zoobenthos			
Hyalella azteca	$SeO_3^=$	5	336-hr LC_{50}: 0.07 mg Se/L Survival and health unaffected at 0.03 mg Se/L
Xenopis laevis	$SeO_3^=$	2	1 mg Se/L eventually lethal after 1 to 10 days of continuous exposure at early gastrula stage
Anodonta sp.	$SeO_3^=$	11	Increased burrowing depth at 1.0 mg Se/L inferred as avoidance behaviour
Lymnae stagnalis L.	$SeO_3^=$	13	7.5 day - LC_{50}: 3 mg Se/L
	$SeO_4^=$	13	6 day - LC_{50}: 15 mg Se/L
Fish			
Brachydanio rerio	SeO_2	10b	Hatching unaffected by 0.5-10 mg Se/L Larval mortalities <1% at 1 mg Se/L
	$SeO_3^=$	10a	Larval 96-hr LC_{50}: 15-23 mg Se/L (95% confidence interval)
	$SeO_4^=$	10a	Larval 96-hr LC_{50}: 81-82 mg Se/L (95% confidence interval)
Carassius auratus	SeO_2	3	Juvenile 96-hr LC_{50}: 36.6 mg Se/L
Catastomus commersonii	$SeO_3^=$	8	96-hr LC_{50}: 29 mg Se/L
Cyprinus carpio	SeO_2	7	5 mg Se/L induced a 2-3% reduction in hatchability 1 mg Se/L did not affect hatchability, but enhanced mercury-induced ($HgCl_2$) mortality at 1 mg Hg/L
Esox lucius	$SeO_3^=$	8	75-hr LC_{50}: 11 mg Se/L
Ictalurus punctatus	SeO_2	3	Juvenile 96-hr LC_{50}: 18.2 mg Se/L
Lepomis macrochirus	SeO_2	3	Juvenile 96-hr LC_{50}: 40.0 mg Se/L; 336 hr LC_1: 8.1 mg Se/L
Perca flavescens	$SeO_3^=$	11	Over course of one month continuous exposure to 1 mg Se/L, progressive death of young of the year observed
	$SeO_3^=$	8	240-hr LC_{50}: 5 mg Se/L
Pimephales promelas	$SeO_3^=$?	5	Fry 96-hr LC_{50}: 1.0 mg Se/L 336-hr LC_{50}: 0.60 mg Se/L
	SeO_2	3	Fry 96-hr LC_{50}: 2.9 mg Se/L Juvenile 96-hr LC_{50}: 7.3 mg Se/L 168-hr LC_1: 0.86 mg Se/L
Salmo gairdneri	$SeO_3^=$	6	Eggs: marginal increase in mortality of eyed eggs at >28 µgSe/L Juvenile (0.8 g) 96-hr LC_{50}: 7.2 mg Se/L 9-day LC_{50}: 3.7-8.0 mg Se/L (95% confidence interval) Suggested that >50 µgSe/L induced sublethal responses such as reduced blood iron and red blood cell volume
		4	96-hr LC_{50}: 2.5 mg Se/L No mortalities observed at 0.1 mg Se/L over 28 days
Salvelinus fontinalis	SeO_2	3	96-hr LC_{50}: 14.3 mg Se/L in adults

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* The list of references is: 1 Bringmann and Kuhn 1959 (seen in 12); 2 Browne and Dumont 1979; 3 Cardwell et al. 1976; 4 GisselNielsen and Gissel-Nielsen 1978; 5 Halter et al. 1980; 6 Hodson et al. 1980; 7 Huckabee and Griffith 1974; 8 Klaverkamp et al., in prep.; Lindstrom and Rodhe 1978; 10a, 10b Niimi and LaHam 1975, 1976; 11 Rudd et al. 1980a; 12 Schultz et al. 1980; 13 Van Puymbroeck et al. 1982.

@ SeO_2 is a solid which when dissolved in water becomes either selenite and or selenate (Huckabee and Griffiths 1974).

? Unclear from original text whether $SeO_3^=$ or $SeO_4^=$ was tested.

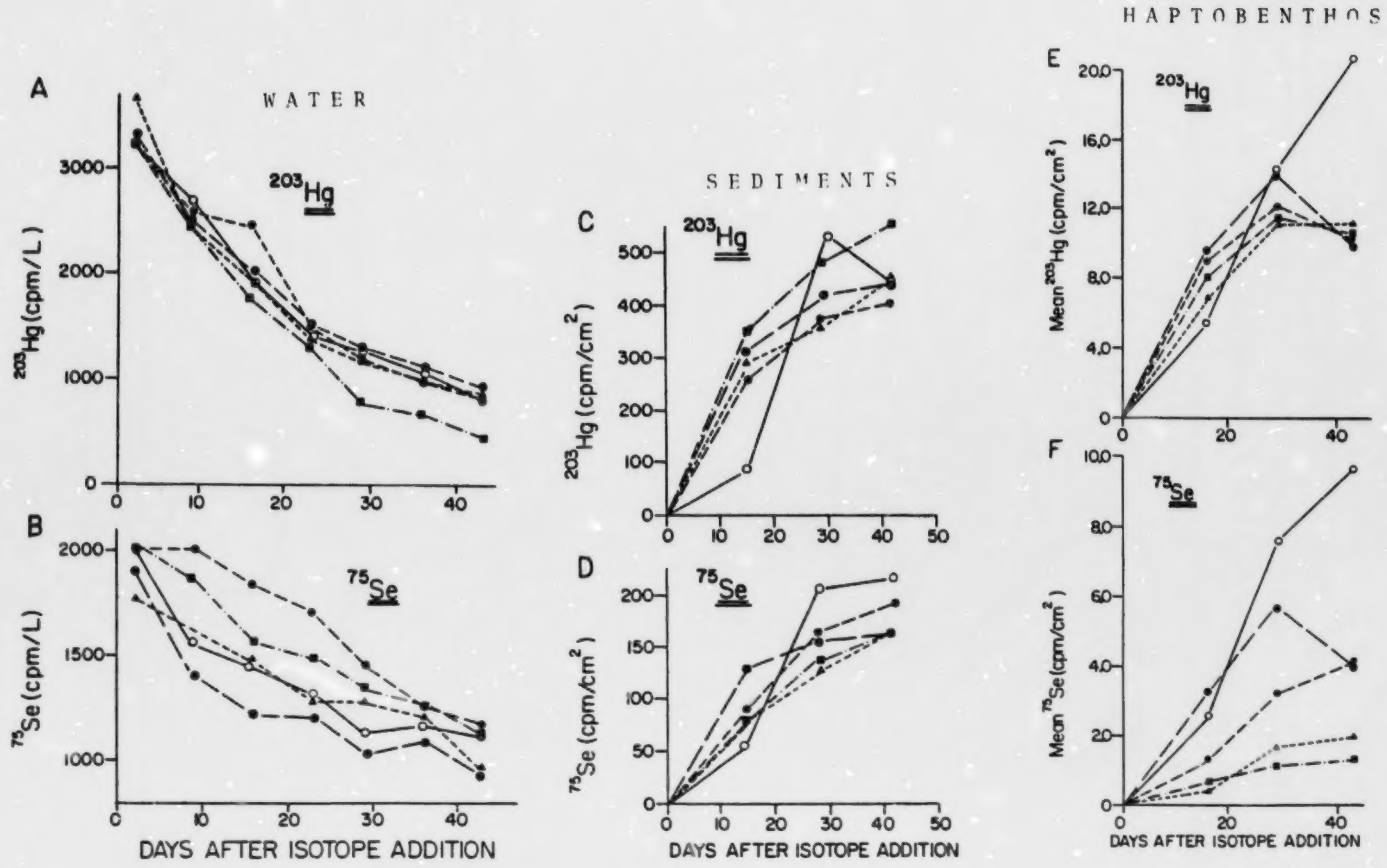

Fig. 1. Movement of ^{203}Hg and ^{75}Se among geochemical compartments in the control (O-one and O-two) and selenium (*-1, Δ-10, -100 µg Se/L) enclosures: loss of ^{203}Hg (A) and ^{75}Se (B) from the water column; accumulation of ^{203}Hg (C) and ^{75}Se (D) in sediments; and accumulation of ^{203}Hg (E) and ^{75}Se (F) in haptobenthos.

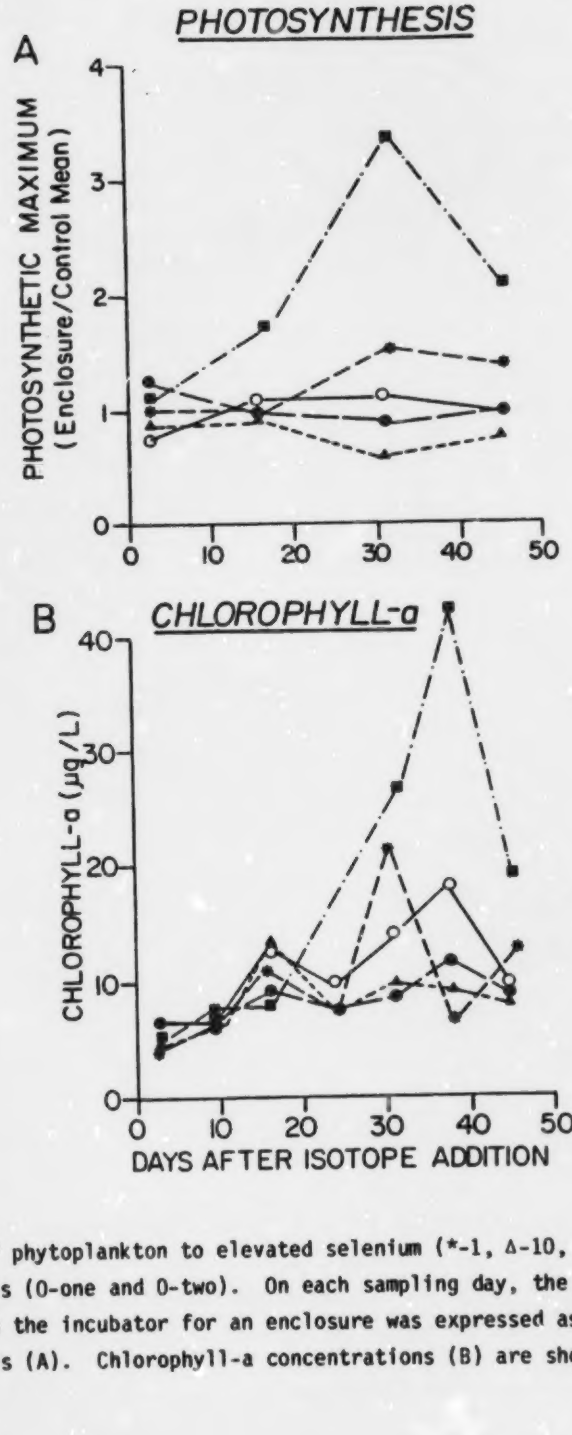

Fig. 2. Response of phytoplankton to elevated selenium (*-1, Δ-10, -100 µg/L) as compared to the controls (0-one and 0-two). On each sampling day, the maximum photosynthetic rate observed in the incubator for an enclosure was expressed as a fraction of the mean of the controls (A). Chlorophyll-a concentrations (B) are shown over time.

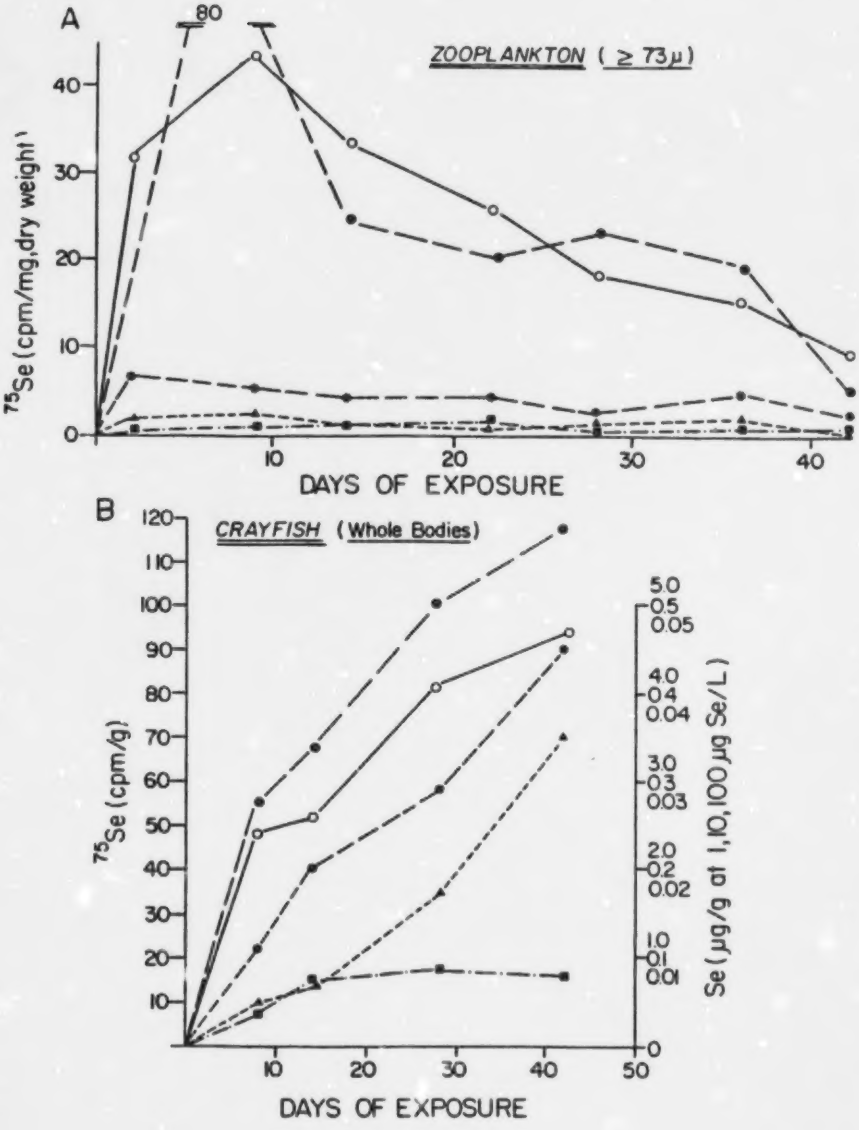

Fig. 3. Accumulation of ^{75}Se in zooplankton (A) and crayfish wholebodies (B) in the control (O-one and O-two) and elevated selenium (*-1, Δ-10 and -100 μg/L) enclosures. Based on the known specific activity of ^{75}Se:Se, actual selenium bioaccumulation could be calculated. Concentrations corresponding to each selenium tube are presented on the right axis of the figure.

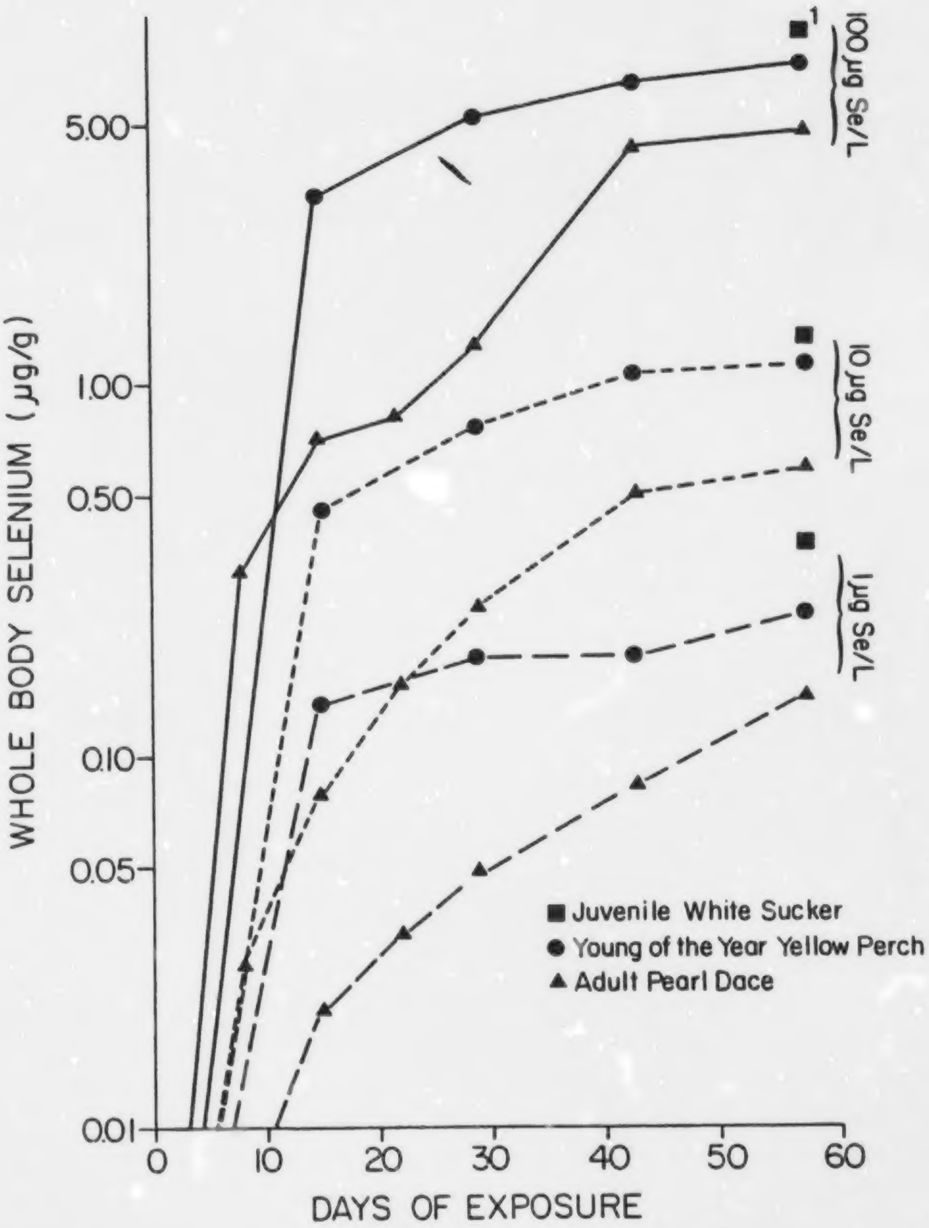

Fig. 4. Bioaccumulation of selenium by three fish species after a single addition of 1, 10 and 100 µg Se/L. Each point usually represents the lognormal mean concentration of six dace, three perch or six suckers.

[1] Only one sucker was retrieved from the 100 µg Se/L enclosure.

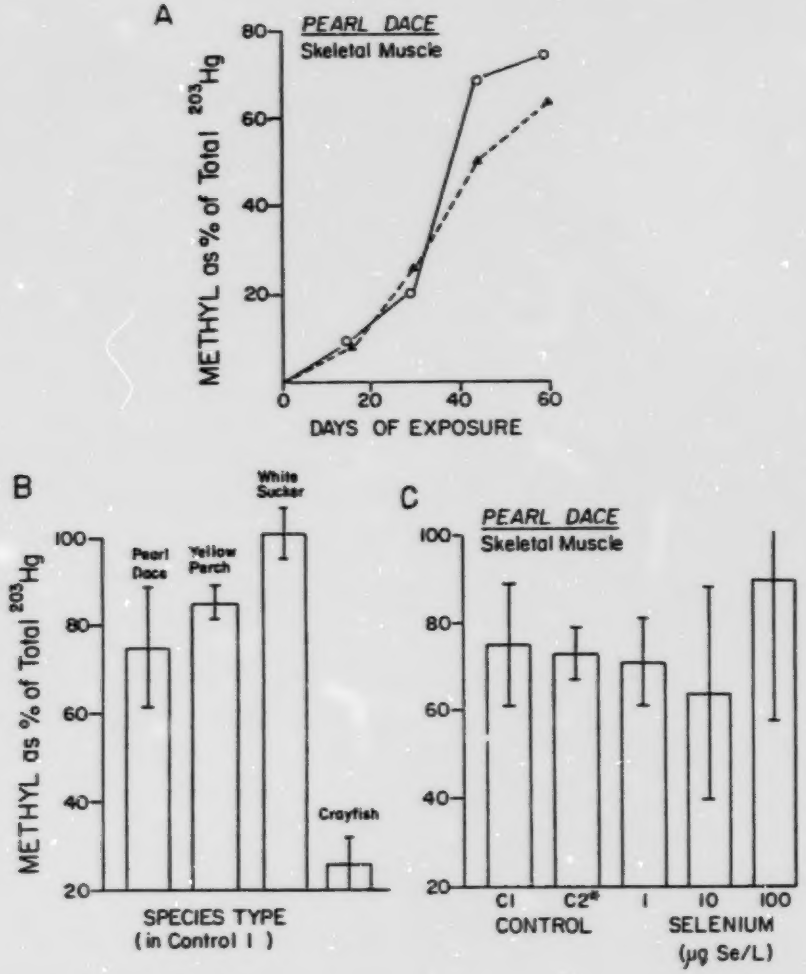

Fig. 5. Methyl ^{203}Hg as a fraction of total ^{203}Hg. Temporal changes in the proportion of total ^{203}Hg present as methyl in skeletal muscle of pearl dace in a control (O-one) and selenium (Δ-10 μg Se/L) enclosure (A). Each point represents the mean of three individuals. The selenium and control conditions do not appear different. The fraction of ^{203}Hg present as methyl in skeletal muscle of dace, perch, sucker and in the abdominal muscle of crayfish after two months exposure in a control enclosure is shown in (B). Standard deviations about the means (n=3) are shown. The proportion of methyl in pearl dace skeletal muscle after two months of exposure in the control and selenium enclosures (C). There is no apparent effect of selenium upon methyl:total. *No dace were retrieved from control two on day 58, so that the mean for control two was extrapolated from the relationship with control one observed on the previous sampling date.

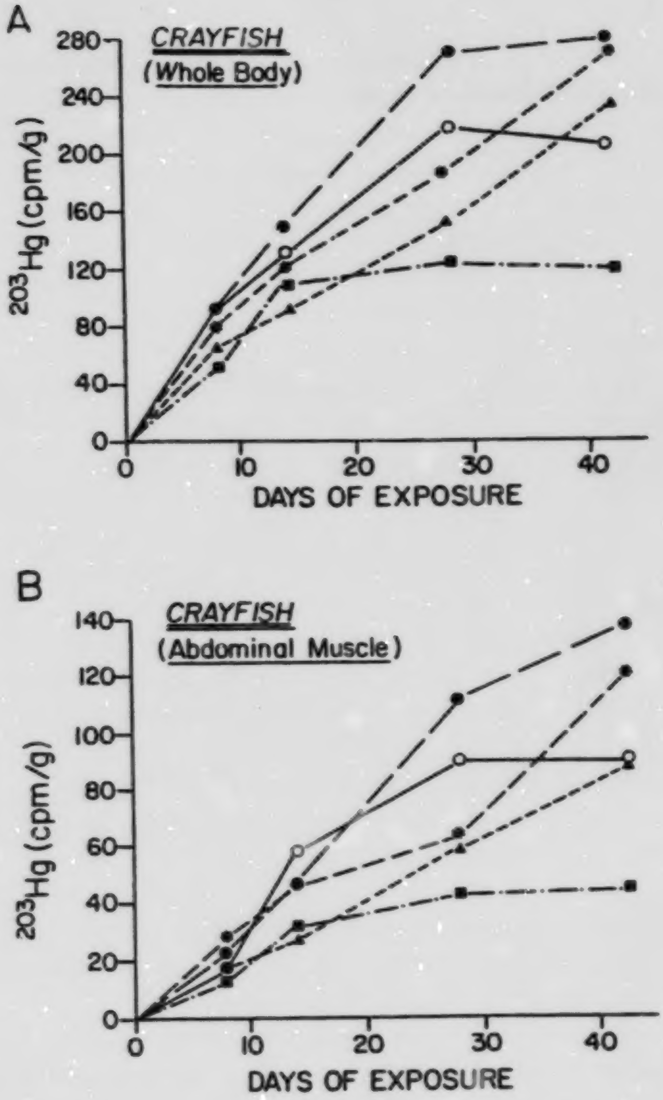

Fig. 6. ^{203}Hg bioaccumulation observed in crayfish whole bodies (A) and abdominal muscle (B) in the control (0-one and 0-two) and selenium (*-1, Δ-10 and -100 µg/L) enclosures.

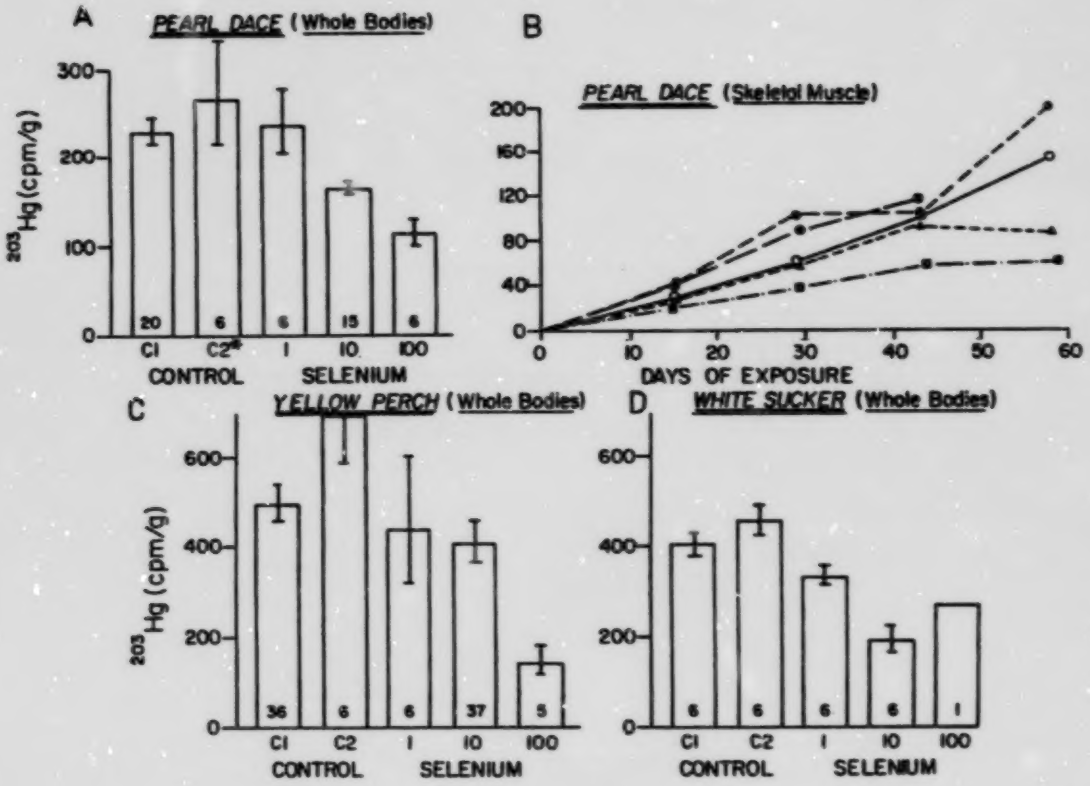

Fig. 7. Lognormal means and 95% confidence limits of ^{203}Hg activities in whole bodies of pearl dace (A), yellow perch (C) and white sucker (D) after two months of exposure in the control (0-one and 0-two) and selenium (*-1, Δ-10 and -100 µg/L) enclosures. The number of individuals comprising each mean is shown at the bottom of each bar. The mean activity of ^{203}Hg in skeletal muscle of pearl dace samples is shown as a function of time in (B). The means shown usually represent four samples. *As described in Fig. 5.

4. INTERFERENCE BY SELENIUM WITH ACCUMULATION OF MERCURY IN AQUATIC FOODWEBS: FISH PREY-PREDATOR EXPERIMENTS

M. A. Turner and A. L. Swick

Selenium can move rapidly from water to sediments when added to aquatic ecosystems at either trace (<0.2 µg Se/L) or elevated concentrations (Hesslein et al. 1980; Jackson et al. 1980; Rudd et al. 1980, section 3), and is bioaccumulated efficiently by aquatic biota at concentrations in water ranging from <0.2 to 100 µg Se/L (Rudd et al. 1980, sections 3 and 8). Although aquatic biota can accumulate both inorganic and organic selenium compounds directly from water (Hodson et al. 1980; Sandholm et al. 1972), laboratory aquarium experiments indicate that the food vector is also important (Sandholm et al. 1973). Experiments in large enclosures have also suggested that food may be the dominant source of selenium for aquatic biota (Rudd et al. 1980). However, experimental demonstration of the relative importance of food and water vectors for selenium bioaccumulation in natural ecosystems is lacking.

When present in mercury-contaminated foodstuffs, selenium may decrease or prevent mercury poisoning in mammals, in spite of frequently increasing the retention of mercury in terrestrial vertebrates (Chang et al. 1977; Friedman et al. 1978; Ganther and Sunde 1974). In short-term aquarium experiments, selenium was added to water (3 mg Se/L) as selenium dioxide. Northern creek chubs (*Semotilus atromaculatus*) were then protected from otherwise toxic concentrations of inorganic mercury (>70 µg Hg/L), but the influence of selenium pretreatment upon subsequent bioaccumulation of mercury was erratic (Kim et al. 1977). Selenium concentrations of 10 and 100 µg Se/L, added as selenite, reduced mercury bioaccumulation in some organisms in aquatic ecosystem experiments (Rudd et al. 1980, section 3), and in white suckers (*Catostomus commersoni*), and possibly in perch (*Perca flavescens*), at 1 µg Se/L. Although 100 µg Se/L increased the rate of movement of ^{203}Hg from water to sediments, neither sedimentation nor chemical speciation of ^{203}Hg were different in 1 or 10 µg Se/L versus control enclosures (section 3). The mechanisms underlying the influence of selenium upon mercury bioaccumulation remain unclear.

It has been suggested that selenium present in atmospheric fallout may reduce the severity of mercury contamination resulting from acid rain (section 3). Careful addition of selenium to watercourses, at low concentrations, has been suggested as an ameliorative procedure for systems contaminated by point source discharges of mercury (Rudd et al. 1980, section 3). So far, however, there is no information available on the role of selenium in fish predator-prey relationships.

This project was conducted as part of a larger research program on the mercury-contaminated Wabigoon River system (Rudd et al. 1980, section 3). Yellow perch and northern pike were used in an *in situ* experiment to assess the role of selenium in prey-predator relationships. Research objectives included assessment of the relative importance of water and food vectors in the bioaccumulation of both mercury and selenium by predaceous fish at both trace and elevated concentrations of selenium in water (<0.2 µg Se/L and ~5 μg Se/L, respectively). Finally, it was to be determined whether added selenium would decrease the transfer of mercury between trophic levels.

METHODS

Radioisotopes were added to each of two 10-meter diameter enclosures (10^5L) located in mercury-contaminated Clay Lake (Armstrong and Hamilton 1973). No chemical additions were made to the control enclosure, while sodium selenite was added to another at an initial concentration of 10 μg Se/L.

Predator-prey experiments were initiated Aug 15, 1979, approximately one month after the selenium mercury-amelioration experiment described in section 3 had begun. General experimental methods, including description of the location and structure of the 10-meter diameter enclosures, are given in section 3 and Rudd et al. (1980).

The initial variability of stable selenium and mercury in the perch and pike would have hindered detecting treatment effects, but with the addition of the radioisotopes ^{203}Hg and ^{75}Se, a definite time zero existed beyond which new accumulations of radioisotopes could be compared between test and control conditions. With the analytical sensitivity of radioisotope techniques, we were able to avoid confounding the experiment otherwise incurred by large chemical additions. It is unlikely however that the radioisotopes added would have equilibrated with their respective stable elements in the fish during the experiment. Further information about radioassay techniques can be found in Rudd et al. (1980) and section 3.

Fish for these experiments were obtained by seining along a nearby beach in Clay Lake. Northern pike (Esox lucius) of ~35 g, and yellow perch (Perca flavescens) of ~2 g, were selected and assigned randomly to experimental treatments.

A major experimental objective was to partition the routes of uptake of isotopic mercury and selenium into food and water vectors. In one experiment (Fig. 1A), predators (young northern pike, Esox lucius) could accumulate ^{203}Hg and ^{75}Se from food (young of the year yellow perch, Perca flavescens), and water, or from water alone. In a corroboratory experiment (Fig. 1B), pike could only obtain radioisotopes by consumption of radiolabelled perch in the absence of radioisotopes in the surrounding water. Each experiment had both control, or trace, and added selenium conditions. Hereafter, the trace selenium situation (<0.2 μg Se/L) will be referred to as the control condition.

In the first experiment (Fig. 1A), there were three cages for each of the control and added selenium conditions placed within their respective 10 meter diameter enclosures. These cages (4' x 4' x 4') were constructed with wooden frames and untreated Ace-style nylon netting (Nichols Net and Twine Co.). In each of the control and added selenium conditions, there were two groups of pike.

All pike could obtain ^{75}Se and ^{203}Hg from water, but in one group pike could also obtain radioisotopes by consumption of radiolabelled perch. After one and two weeks, three individual pike were sampled from each treatment combination for whole body and tissue isotope activities. Isotope activities in whole bodies of perch were also determined in three perch for each combination of selenium (control or added selenium) and duration (one, two or three weeks exposure). The exposure of perch to isotopes began one week prior to initiation of pike exposure. The nominal food ration for each pike was four perch per week. The number of perch remaining in each cage at the end of a sampling period was determined so that the nominal ration could be adjusted accordingly.

For the corroboratory experiment (Fig. 1B), two cages (described above) were placed outside the 10 meter diameter enclosures, each within a larger cage of wire mesh. In absence of exposure to isotopes added to the surrounding water during this corroboratory experiment, pike were fed perch which had been labelled previously with ^{203}Hg and ^{75}Se for two weeks. The nominal ration was three perch/pike. Perch in the added selenium condition were approximately 0.8 μg Se/g (wet weight). Pike were sampled six days later after all perch had been consumed.

Fish were frozen using dry ice immediately after sampling. Samples were kept frozen until dissection into several tissues: dorsal skeletal muscle, liver, gill (including arch), skin, gastrointestinal musculature; and carcass (whole body excluding other tissues). Gastrointestinal contents were extruded from the gut musculature, and collected as a separate sample, but were not included in estimates of whole body activities. Activity in gastrointestinal contents was excluded from estimates of isotope consumed. The gut musculature was rinsed with tap water and prepared separately for radioassay. Samples were then refrozen until radioassay.

Isotope activities in whole bodies of pike and perch, and proportions of isotopes in tissues of pike were examined using factorial analysis of variance (Snedecor and Cochran 1967).

Isotope activities in whole bodies of pike, excluding gastrointestional contents, were determined from activities in observed tissues and carcass samples. Lognormal means and variances were then calculated for each group of pike or perch. To determine the efficiency of absorption of each isotope from food, and to account for any differences in amount of isotope between perch in the selenium and control conditions, "assimilation efficiencies" (Aoyama and Inoue 1973) were calculated:

$$\text{Assimilation efficiency} = \frac{(\text{total isotope consumed}) - (\text{excretion})}{(\text{total isotope consumed})}$$

$$= \frac{(\text{residual isotope in body of pike})}{(\text{total isotope consumed})}$$

$$= \frac{(\text{mean weight of all pike}) \times (\text{mean amount of isotope in whole body of pike obtained from food}^{*})}{(\text{mean \# of perch consumed/pike}) \times (\text{mean isotope burden in perch whole bodies}^{**})}$$

The assimilation efficiency reported for week two represents a mean for the two-week period.

* Accumulation of isotope from food and water were assumed to be independent processes. This has been confirmed experimentally for uptake of methyl mercury in rainbow trout (*Salmo gairdneri*) (Phillips and Buhler 1978). Mercury-203 and ^{75}Se observed to accumulate in the "water-only" group were subtracted from the "food plus water" group to yield an estimate of the contribution due to food alone.

** Weekly isotope activities in perch were calculated as the arithmetic mean of the activities observed at the beginning and end of that week. No correction was made for isotope activity remaining in the gastrointestinal system of the perch.

RESULTS

Selenium. Temporal changes in activity of ^{75}Se in the water column were different between control and stable selenium addition enclosures (Fig. 2A). In the control enclosure, activity was relatively constant at approximately 1125 cpm/L during the three weeks of the experiment. In the selenium enclosure, ^{75}Se activities declined from 1275 to 900 cpm/L, with corresponding total selenium concentrations of ~6.4 and 4.5 μg Se/L.

Chemical speciation of selenium (described more fully in section 3) was also different between these two enclosures. In the control enclosure, ~60% of ^{75}Se was associated with nonpolar dissolved organics (activated charcoal fraction), and to a lesser extent present in ionic or particulate form (about 25 and 15 percent, respectively). In the selenium enclosure, ionic species predominated (~70%), with the remainder associated largely with nonpolar dissolved organics.

Selenium-75 in perch increased rapidly throughout the three week period in both conditions, although there is a suggestion of a lag in uptake during the first week of exposure (Fig. 2B), especially noticeable in the selenium condition. Differences in specific activity (^{75}Se:Se) prevent meaningful comparisons of perch ^{75}Se activities between the control and selenium enclosures.

In the control situation, ^{75}Se activities in pike allowed to feed on ^{75}Se-labelled food, were much greater ($P<0.001$) than in the condition where ^{75}Se was supplied in water only (Fig. 2C-control). Therefore, at trace concentrations of selenium in water (<0.2 μg Se/L), the food vector appears to be the dominant route for bioaccumulation of selenium. With increased concentrations of selenium in water, the relative importance of water for accumulation of ^{75}Se was substantially increased (Fig. 2C-selenium). This was attributable to reduced efficiency in assimilation of selenium from foodstuffs in the presence of increased concentrations in water (Fig. 2D-selenium:food + water versus food). In the control, assimilation of selenium from food (perch) was approximately 30%, whereas assimilation ranged from 8 to 19% with the addition of selenium (Fig. 2D-food + water:control versus selenium). When selenium was increased in food but not in water, as in the corroboratory experiment (Fig. 1B), the assimilation efficiency was not very different from that in the control (Fig. 2D-food only).

Partitioning of selenium among the tissues sampled, as indicated by tissue: whole body activities (Table 1), was not altered greatly by either the amount of selenium present (control versus selenium), or the route of selenium uptake (water versus food and water). In all treatments, the proportion of ^{75}Se was highest in the liver (5.8 to 15.0), and lowest in the skeletal musculature (0.21 to 0.41). The proportion of ^{75}Se in the gut musculature was somewhat higher in pike fed ^{75}Se-labelled food than in pike with access to ^{75}Se in water only ($P<0.01$). This increase was reduced in the presence of elevated selenium concentrations in water (Table 1), which is consistent with the observation of reduced dietary assimilation (Fig. 2D-food + water:control versus selenium).

Mercury-203. Activities of ^{203}Hg in water were similar in both control and selenium enclosures, decreasing to one-half during the experiment (Fig. 3A). There were no substantial differences in partitioning of ^{203}Hg among the different chemical fractions (described more fully in section 3): particulate (>0.45 μ), nonpolar dissolved organics, ionic and undefined.

Throughout the main experiment (Fig. 1A), ^{203}Hg in whole bodies of perch continued to increase in both the control and added selenium enclosures (Fig. 3B). Mercury-203 activities in selenium-exposed perch were consistently lower than in control perch ($P = 0.02$).

Where mercury and selenium isotopes could be taken up directly from water only, ^{203}Hg activities in whole bodies and skeletal muscle of pike were not different between the control and selenium conditions (Fig. 3C-water only). Where ^{203}Hg could also be accumulated by consumption of perch, activities in whole bodies ($P<0.03$) and skeletal muscle ($P=0.001$) of pike were always lower in the presence of added selenium (Fig 3C-food + water). Increased selenium reduced the efficiency of accumulation of ^{203}Hg from foodstuffs from approximately 15% in the control to 5-11% in the presence of added selenium (Fig. 3D-food + water). In the corroboratory experiment (Fig. 1B, isotopes and added selenium present only in food), a reduction in assimilation efficiency of ^{203}Hg of similar magnitude was also observed (Fig. 3D-food only), suggesting that selenium in food rather than selenium in water appears responsible.

Where ^{203}Hg could be taken up only from the water column, waterborne selenium did not influence partitioning of ^{203}Hg among pike tissues (Table 2) - not even in gill tissue. In contrast, where ^{203}Hg could also be accumulated from food, the proportion of ^{203}Hg in both the gut ($P<0.001$) and skeletal musculature ($P=0.001$) was higher than where ^{203}Hg could be taken up only from water. These increases were reduced during exposure to selenium ($P<0.01$ and $P<0.05$, respectively).

DISCUSSION

Selenium bioaccumulation. Selenium is accumulated from both food and water (Fig. 2C, Table 1). The type of organism, food and water concentrations and respective chemical speciation determine the relative importances of the routes.

At low concentrations of selenium in water (<0.2 μg Se/L), foodweb transfers predominate for fish (Fig. 2C, Rudd et al. 1980; Sandholm et al. 1973), although concentrations in other organisms, such as in zooplankton, are sensitive to water concentrations (section 3). At increased concentrations in water (Fig. 2A, 4.5-6.4 μg Se/L), when selenium is present largely as anion (section 3), pike accumulated somewhat less ^{75}Se from the water column (Fig. 2C-water only: control versus selenium); although the ambient concentration of radioisotope was lower (Fig. 2A). The greater than twenty-five-fold increase in selenium water concentration (<0.2 versus ~5 μg Se/L) indicates that substantially more selenium was accumulated.

Fish seem able to regulate the amount of selenium bioaccumulated to at least a limited extent. Although the efficiency of assimilation of selenium from food appears independent of food selenium concentration (Fig. 2D: food only), increased concentrations of selenium in water can reduce assimilation of selenium from food (Fig. 2D-food + water:control versus selenium). Conversely, food concentrations do not influence accumulation from the water column (Hilton and Hodson submitted).

Selenium concentrations vary among tissues (Table 1; Hodson et al. 1980, sections 3 and 8) and partitioning can vary with time (e.g., Table 1 - liver:week one versus two). Highest concentrations are observed in the liver (Table 1) and kidney, both of which have been postulated to be involved with selenium regulation and excretion (Hodson et al. 1980).

Interaction between selenium and mercury. Caged yellow perch, which presumably accumulated radioisotopes from both food (zooplankton) and water, consistently accumulated less ^{203}Hg when exposed to added selenium (Fig. 3B). This was characteristically observed in pearl dace (*Semotilus margarita*), white suckers (*Catostomus commersoni*), and other perch living within the 10 meter diameter enclosure with an initial water concentration of 10 µg Se/L (section 3). When selenium was increased only in the water column (4.5-6.4 µg Se/L, Fig. 2A), there was no change in the amount of ^{203}Hg that pike accumulated from water (Fig. 3C-water only). Because the proportion of methyl to total mercury in water was probably small, circa 5% (Parks et al. 1980), this effect may also be seen as a lack of action of selenium upon uptake of inorganic mercury from water. At a higher concentration of selenium, added initially as selenite ($SeO_3^{=}$, 100 µg Se/L), a more rapid movement of ^{203}Hg from water to sediment was also noted (Rudd et al. 1980, section 3), possibly reducing uptake of ^{203}Hg via food.

Control pike were able to accumulate ^{203}Hg from both water and food obtained from 33% (week 1) to 43% (week 2) of their ^{203}Hg burden from food (Fig. 3C-control; water only versus food + water). In both weeks, an assimilation efficiency of ≈15% was observed for the transfer of ^{203}Hg from perch (food) to pike (Fig. 3D-control). This is similar to the observation by Phillips and Gregory (1979) in which pike assimilated 19% of naturally occurring methyl mercury in young of the year carp (*Cyprinus carpio*). In contrast, when selenium concentrations were increased in perch (0.05-0.4 µg Se/g, Fig. 2B), assimilation of ^{203}Hg from food decreased to between 5 and 11% (Fig. 3D-food and water:selenium). This was corroborated in the food-only experiment (Fig. 3D-food only:selenium) when selenium levels in perch were about 0.8 µg Se/g (wet weight). These observations imply that the reduction in bioaccumulation of ^{203}Hg by fish, observed in *in situ* ecosystem experiments (section 3, Rudd et al. 1980), is due to interference of selenium with mercury mobilized through foodwebs, rather than upon mercury bioaccumulated directly from water.

Control pike had proportionately more ^{203}Hg in the gut and skeletal musculatures when accumulating ^{203}Hg from food and water together, than from water only (Table 2). This is consistent with the observation that mercury burdens obtained via food and water are additive (Phillips and Buhler 1978). With increased concentrations of selenium in both food and water, there was a greater proportion of ^{203}Hg found in the liver in week two ($P = 0.01$), with comparatively less in the skeletal ($P < 0.05$) and gut musculatures ($P < 0.01$; Table 2-food + water: control versus selenium, week two). This liver ^{203}Hg would probably have been inorganic (Burrows and Krenkel 1973), so that the comparison between ^{203}Hg burdens of control and selenium-exposed pike (Fig. 3C), could underestimate the influence of selenium upon body burdens of methyl mercury. Increased activities of ^{203}Hg in liver may also be the result of enhanced demethylation occurring within the liver as suggested by Burrows and Krenkel (1973). Interestingly, the liver was also a site for high selenium concentrations (Table 1); and may be related to binding of mercury by a selenium-containing metallothionine (J. Klaverkamp, pers. comm.).

Implications for amelioration strategies. Selenium supplementation has been postulated as a stratagem to reduce point-source mercury contamination (Rudd et al. 1980, sections 1 and 3). The results of these experiments support this idea and provide further insights into both the mode of application and effectiveness of selenium supplementation in aquatic ecosystems.

Selenium in water has little or no impact upon mercury bioaccumulation from water (Fig. 3C), and its action appears to be exerted at the level of food intake. Because selenium is transferred efficiently through foodwebs (Fig. 2D; Rudd et al. 1980), elevated water concentrations would not have to be maintained continuously if periodic pulses could sufficiently inoculate the foodweb. It is possible that manipulation of concentrations in the surface floc of sediments (section 1) would be an appropriate strategy, rather than manipulating concentrations in water per se.

Selenium can reduce bioaccumulation of mercury in several fishes (Fig. 3B, C and D; Rudd et al. 1980, section 3). This interference may be increased further in organisms at "higher" positions within foodwebs; i.e., selenium may interfere with the biomagnification of mercury. For example, the lowered ^{203}Hg activities observed in perch (Fig. 3B) appear to be further reduced by the lowered assimilation of ^{203}Hg from food (perch) by pike (Fig. 3D: selenium versus control). Additionally, the selenium-induced reduction of ^{203}Hg in skeletal muscle of pike (36% of control, Fig. 3C: food and water) appears to be an amplification of the decrease in skeletal muscle of pearl dace (58% of controls) exposed for two months to selenium initially at a concentration of 10 μg Se/L (section 3). This suggestion of interference with the transfer of mercury, depending upon foodweb position, is further corroborated by observations of decreased bioaccumulation of ^{203}Hg in predaceous aquatic insect larvae (Sialis and Chaoborus) living in ecosystems containing added selenium (initially at 10 and 100 μg Se/L; whereas, no decrease was apparent in detrivorous insects (Hexagenia and Chironomus) (B. Townsend, pers. comm.). Therefore, the reduction in accumulation of ^{203}Hg in young suckers and possibly in perch, but not dace, observed after two months at 1 μg Se/L (section 3), may be observed consistently in predaceous fish of foodwebs larger than those experimentally manipulated to date. For selenium to exert its mercury-detoxifying effect, however, levels of mercury do not have to be reduced either in the contaminated foodstuff or in the consumer (Chang et al. 1977; Friedman et al. 1978).

A long term study of experimental addition(s) of selenium to a whole lake would be a logical research step prior to the use of selenium as an ameliorating agent. In addition to further work on ecosystem toxicology and dose-response relationships future research should determine whether elevated selenium concentrations in water only can influence assimilation of mercury from foodstuffs, and what minimum ratio of selenium:mercury in food is required to reduce assimilation of mercury.

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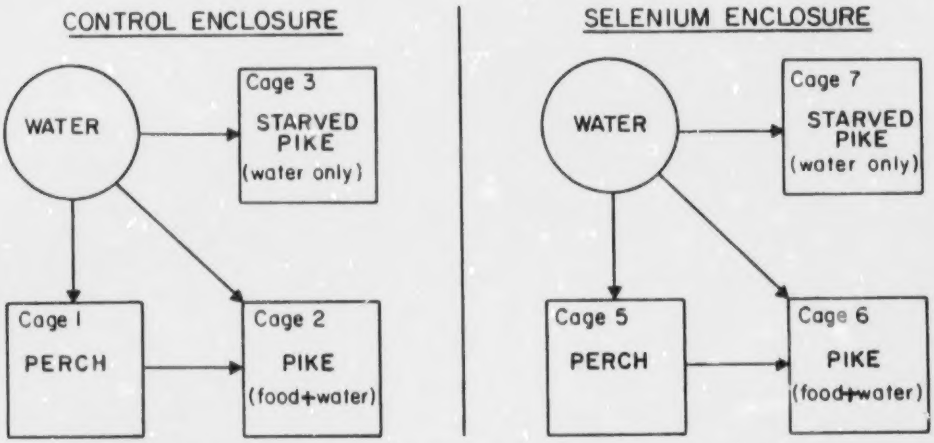
Table 1. Ratios of tissue to whole body activities of ^{75}Se (mean ± SD, n=3).

Tissue	Experimental Condition	Week One		Week Two	
		Water	Food & Water	Water	Food & Water
Gill	Control	5.98 (±1.56)	4.37 (+1.04)	4.31 (±0.74)	3.25 (±0.19)
	Selenium	5.66 (±2.49)	6.44 (±1.17)	4.86 (±2.12)	4.81 (±2.45)
Skin	Control	1.85 (±0.60)	2.16 (±0.13)	1.67 (±0.52)	1.57 (±0.17)
	Selenium	Not Measured	0.97 (±1.37) n=2	0.80 (±0.53)	1.15 (±1.01)
Gut	Control	1.77 (±0.92)	4.05 (±0.87)	1.98 (±0.65)	3.10 (±0.65)
	Selenium	2.29 (±1.03)	2.82 (±0.15)	2.02 (±0.76)	1.80 (±0.35)
Liver	Control	7.80 (±3.24)	7.37 (±1.22)	9.27 (±2.76)	8.51 (±0.89)
	Selenium	10.84 (±3.24)	5.76 (±5.29)	14.96 (±7.51)	8.75 (±0.89)
Muscle	Control	0.21 (±0.15)	0.23 (±0.04)	0.34 (±0.07)	0.38 (±0.13)
	Selenium	0.41 (±0.35)	0.27 (±0.24)	0.21 (±0.19)	0.40 (±0.04)

Table 2. Ratios of tissue to whole body activities of ^{203}Hg (mean + SD, n=3).

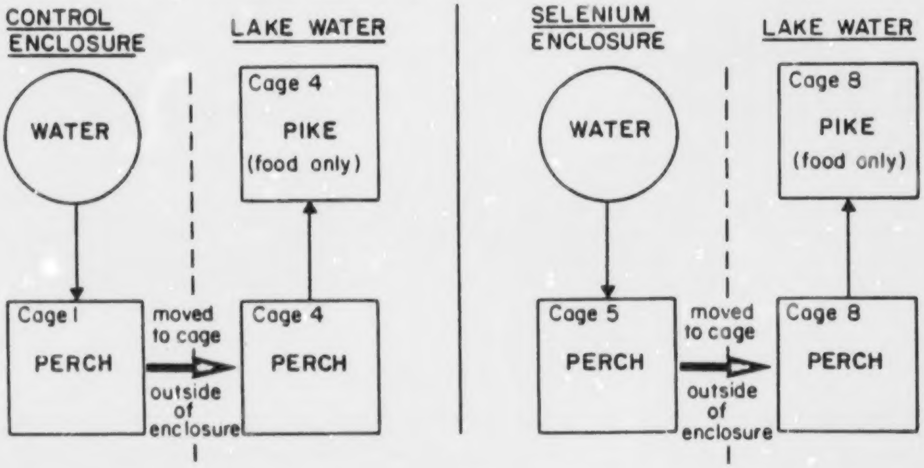
Tissue	Experimental Condition	Week One		Week Two	
		Water	Food & Water	Water	Food & Water
Gill	Control	9.49 (±1.49)	8.80 (±1.84)	9.07 (±1.68)	4.39 (±0.23)
	Selenium	9.96 (±1.67)	10.79 (±1.16)	5.19 (±3.01)	7.40 (±1.95)
Skin	Control	1.08 (±0.50)	1.26 (±0.34)	1.24 (±0.57)	0.64 (±0.10)
	Selenium	Not Measured	0.59 (+0.83, n=2)	0.76 (+0.37)	0.93 (± 0.88)
Gut	Control	1.01 (±0.45)	3.36 (±0.78)	0.96 (±0.15)	3.30 (±0.49)
	Selenium	1.10 (±0.49)	2.56 (±0.45)	1.23 (±0.03)	2.03 (±0.61)
Liver	Control	7.95 (±2.21)	7.33 (±1.70)	9.78 (±2.21)	5.73 (±0.27)
	Selenium	7.84 (±1.12)	4.09 (±3.69)	15.33 (±5.26)	8.77 (±0.26)
Muscle	Control	0.10 (±0.05)	0.27 (±0.01)	0.18 (±0.06)	0.55 (±0.00)
	Selenium	0.14 (±0.12)	0.19 (±0.17)	0.20 (±0.18)	0.28 (±0.11)



A. MAIN EXPERIMENT-

^{203}Hg and ^{75}Se available to pike in water and food or in water only

CONTROL ENCLOSURE
WATER
Cage 3
STARVED PIKE
(water only)
Cage 1
PERCH
Cage 2
PIKE
(food+water)
SELENIUM ENCLOSURE
WATER
Cage 7
STARVED PIKE
(water only)
Cage 5
PERCH
Cage 6
PIKE
(food+water)

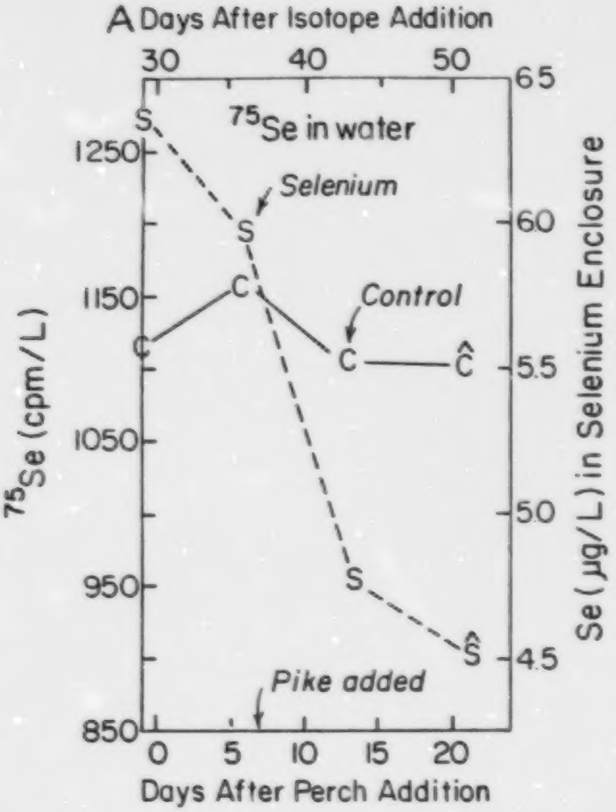


B. CORROBORATORY EXPERIMENT-

^{203}Hg and ^{75}Se available to pike in food only

CONTROL ENCLOSURE
LAKE WATER
WATER
Cage 4
PIKE
(food only)
Cage I
PERCH
moved to cage
outside of enclosure
Cage 4
PERCH
SELENIUM ENCLOSURE
LAKE WATER
WATER
Cage 8
PIKE
(food only)
Cage 5
PERCH
moved to cage
outside of enclosure
Cage 8
PERCH

Fig. 1. Schematics of experimental designs. In the upper panels (A), pike can accumulate ^{203}Hg and ^{75}Se from food and water, or from water only, in the presence or absence of added selenium. In the lower panels (B), isotopes are accumulated only by consumption of prey (perch). Arrows represent main routes of radioisotope movement. It is probable that perch accumulated isotopes from unknown food sources as well as from water directly.



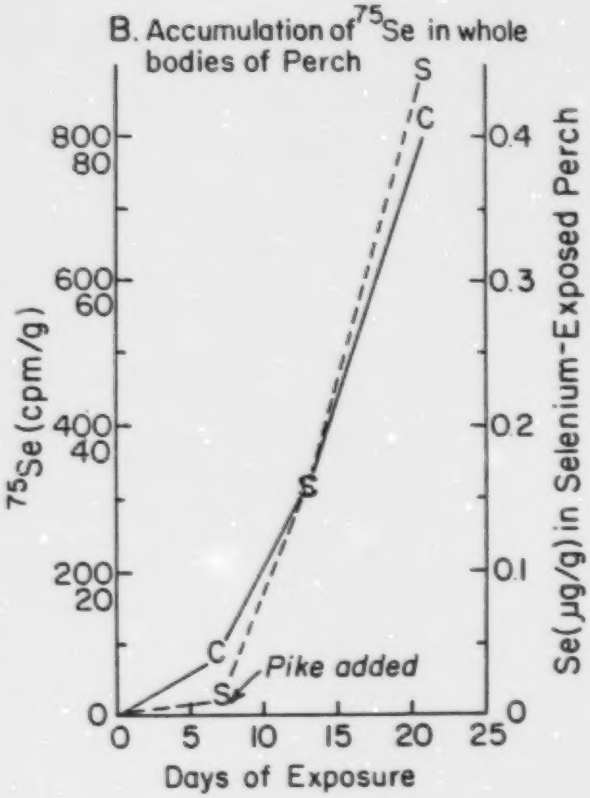
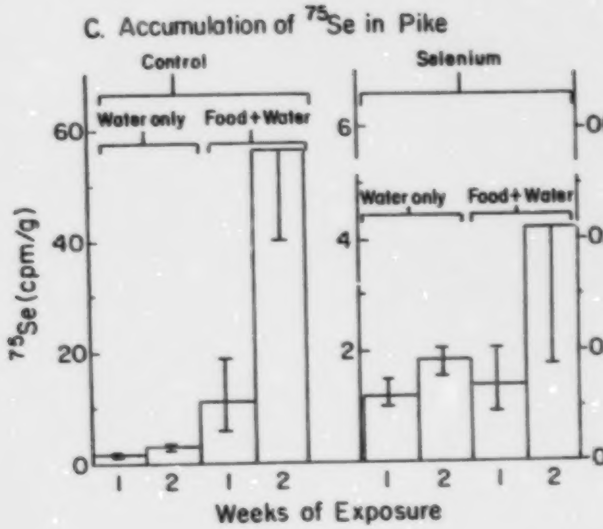


Fig. 2A. Selenium-75 activity in the water columns of the control and selenium enclosures during the periods when fish were exposed to ^{75}Se. Activities shown for the last point are predictions from models fit to earlier data (explained section 3).

Fig. 2B. Selenium-75 activities in whole bodies of perch held in the control (C) or selenium (S) enclosures. Each point represents the antilog of the lognormal mean of three individuals. Along the radioisotope axis (left-hand axis), upper and lower values refer to perch in the control and selenium conditions, respectively. Given the known specific activity of ^{75}Se:Se in the selenium enclosure, computed amounts of selenium accumulated are also shown (right-hand axis).



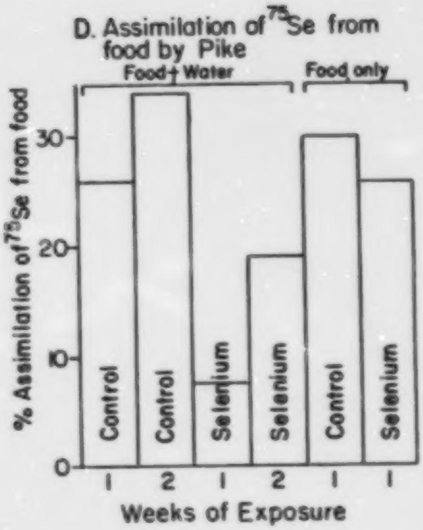


Fig. 2C. Whole body ^{75}Se in northern pike held for one or two weeks in the control or selenium enclosures. Pike were able to accumulate ^{75}Se from food (perch) and water, or from water only. Two standard error bars are shown about each mean of three individuals. The right-hand axis is as described in Fig. 2B.

Fig. 2D. Efficiency of assimilation of ^{75}Se from food (perch) in the gut of pike after one and two weeks. To obtain the estimate of the body burden of ^{75}Se due to food alone, the uptake of ^{75}Se from water, as measured in the water-only condition (Fig. 2C), was subtracted from the body burdens observed in the food and water condition. In the corroboratory, food-only experiment, the contribution of isotopes in food to the body burden was observed directly.

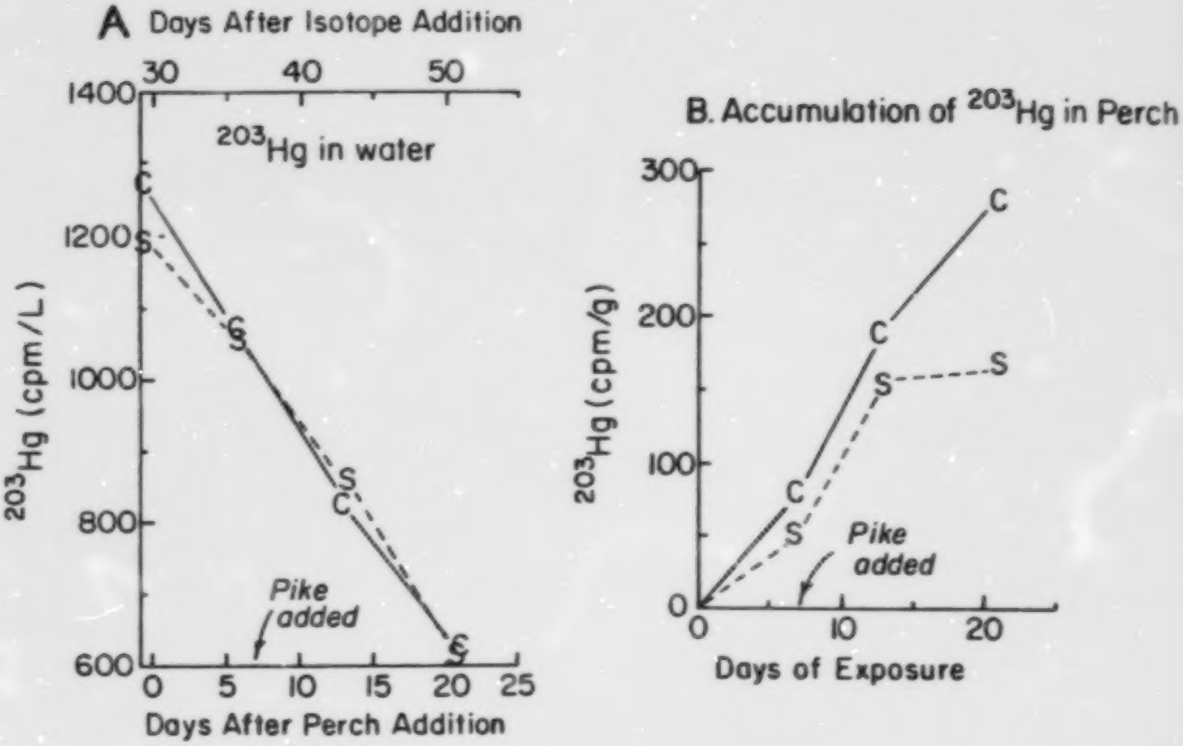
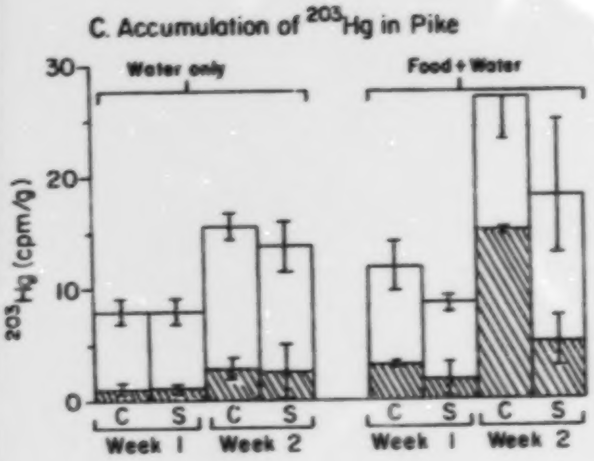


Fig. 3A. Activities of ^{203}Hg in the water column of the control (C) and selenium (S) enclosures during the periods when perch and pike were exposed to ^{203}Hg. Activities shown for the last point are derived from model predictions (explained in section 3).

Fig. 3B. Mercury-203 in whole bodies of perch held in either the control (C) or selenium (S) enclosures. Each point represents the antilog of the lognormal mean, usually of three individuals. Activities of ^{203}Hg in perch of the selenium and control conditions were significantly different ($P = 0.02$).



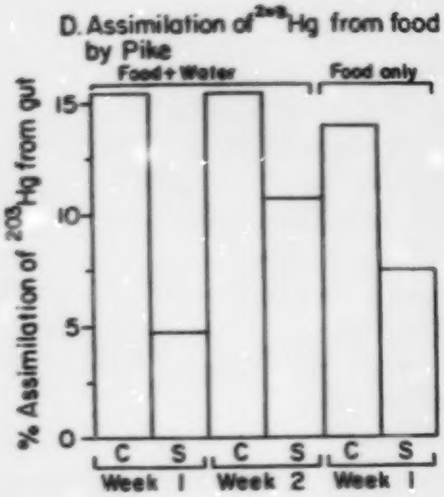


Fig. 3C. Activities of ^{203}Hg in whole bodies of northern pike held for one or two weeks in the control (C) or added selenium (S) conditions. Pike were able to accumulate ^{203}Hg from food (perch) and water, or by uptake from water only. Activities in skeletal muscle are shown in the hatched area, while those in whole bodies are represented by the total height of each bar. Two standard error bars are shown about each mean of three individuals.

Fig. 3D. Efficiency of assimilation of ^{203}Hg from food (perch) in the gut of pike after one and two weeks. To obtain the estimate of the burden of ^{203}Hg due to food alone, the uptake of ^{203}Hg from water, as measured in the water only condition (Fig. 3C), was subtracted from the body burdens observed in the food and water condition. In the corroboratory, food-only experiment, the contribution of isotopes in food to the body burdens was observed directly.

5. MERCURY AND SELENIUM BIOACCUMULATION AS A FUNCTION OF AQUATIC PRIMARY PRODUCTIVITY

J. W. M. Rudd and M. A. Turner

INTRODUCTION

The ways in which mercury from the environment can accumulate in fish (often to levels potentially toxic to humans) are only partially understood. More knowledge is needed on factors controlling rates of mercury bioaccumulation. This knowledge would be especially useful in designing methods to ameliorate the problem. One factor which may be important in controlling fish mercury concentration is ecosystem primary productivity. Primary production rate determines the level of activity of bacterial decomposers, and increasing the rate of supply of bacterial food has been found to stimulate mercury methylating activity by natural microbial communities (e.g. section 6). This stimulation of primary productivity might increase fish mercury concentration by elevating methyl mercury concentrations in fish food and water. Alternatively, stimulation of primary production could tend to reduce fish methyl mercury concentration, because the mercury is diluted by faster fish growth rate, and because of increases in lake water pH which promotes the formation of dimethyl mercury (Jernelov et al. 1975, 1976; Beijer and Jernelov 1979; Fagerstrom and Jernelov 1972). Dimethyl mercury is more volatile than monomethyl mercury and it may tend to be lost to the atmosphere rather than be bioaccumulated.

During 1979, we carried out an experiment designed to test the effect of primary production rate on mercury bioaccumulation by fish. The experiment was done in large (10^5 liter) enclosures situated in Clay Lake (50°03'N, 93°30'W), which is part of the mercury polluted English-Wabigoon River system of northwestern Ontario (Armstrong and Hamilton 1973; Scott and Armstrong 1972; Scott 1974; and Armstrong and Scott 1979). Rates of mercury bioaccumulation by fish and other members of the food chain in control enclosures were compared to bioaccumulation rates of the same organisms in test enclosures which had received additions of nitrogen and phosphorus nutrients to stimulate primary productivity.

The effect of primary production rate on selenium bioaccumulation was also followed in this experiment. While selenium is toxic at high concentrations, in trace quantities it has the potential of ameliorating atmospheric or point source heavy metal toxicity problems in the aquatic environments (Rudd et al. 1980; section 3, 4). For example, the element is a known antagonist to the toxic action of mercury (Friedman et al. 1978; Ohi et al. 1976; Frost and Lish 1975; and Ganther and Sunde 1974) and its presence has also been implicated in the reduction of the rate of fish mercury bioaccumuation (Rudd et al. 1980; Speyer 1980; sections 3, 4). Because both of these potentially beneficial selenium effects are dependent upon selenium bioaccumulation through the food chain (Rudd et al. 1980; sections 1, 3, 4), knowledge of the effects of varying primary productivity rates on bioaccumulation of selenium is necessary.

METHODS

The experiments were conducted in four 10 meter diameter, 1.5 m deep, cross-laminated polyethylene enclosures. Their construction was similar to that described in Rudd et al. (1980) except that the enclosures had water tight cross-laminated polyethylene bottoms. The collapsed enclosures were filled by pumping Clay Lake surface water over a three day period. Pumps were moved from enclosure to enclosure on a regular schedule to ensure that the water in all of the enclosures was as similar as possible. Four enclosures were used for this experiment. Two of the enclosures were duplicate experimental controls. The third and fourth enclosures were fertilized, at different rates, with NaH_2PO_4 and $NaNO_3$ (Table 1).

Enclosure Treatments

On day zero, each of the enclosures received approximately 5.7 mCi $^{203}Hg(NO_3)_2$ (which included ~15 µg/L of carrier Hg) and about 1.4 mCi of $H_2{}^{75}SeO_3$ (New England Nuclear; Table 1). A single addition of foodgrade NaCl was made to each enclosure so that leakage could be monitored. Chloride concentrations were approximately twice pre-addition levels, and were assayed by the methods described in Stainton et al. (1977). No leakage was detected during the course of the experiments.

The two control enclosures received no other chemical additions. Two other enclosures (low nutrient and high nutrient) were fertilized with NaH_2PO_4 and $NaNO_3$ (reagent grade, BDH, Table 1). Fertilization commenced 10 days before day zero, the day of isotope addition. Fertilization rates were highest before day zero (Table 1) to maximize the effect of enhanced primary productivity on the food web after addition of the mercury and selenium isotopes.

Radioactive Sampling and Analyses

Water samples were analysed for ^{203}Hg and ^{75}Se speciation as in Hesslein et al. (1980) and Rudd et al. (1980). The particulate fraction was obtained by sequential filtration through GFC-Whatman and 0.45 µm Millipore filters. Then the filtrate was passed through an activated charcoal column to obtain the fraction associated with organic material. This was followed by passage through a mixed cation-anion exchange column (Dowex 1x8, 100-200 mesh and 50W-12 100-200 mesh) to remove the ionic fraction of the radioisotopes. Finally any remaining or unassociated ^{203}Hg was precipitated as ^{203}HgS after oxidation to Hg^{2+} as described in Rudd et al. (1980).

Bioaccumulation of radioisotopes by free-swimming pearl dace (*Semotilus margarita*) and caged crayfish (*Orconectes virilis*) in the control and nutrient enclosures was followed on a fixed sampling schedule. Skeletal muscle was sampled from four dace in each enclosure 10 and 26 days after isotope addition. The crayfish were fed an excess of white sucker flesh which had a mercury concentration of ~0.2 µg/g.

Bioaccumulation of ^{203}Hg and ^{75}Se by the haptobenthos was followed by suspending several uncolonized cross-laminated polyethylene strips from the surface to one meter depth in each enclosure. After radioactive analyses of the strips the haptobenthos was scraped off the polyethylene, dried at 60°C and weighed.

Zooplankton samples (i.e. particulate material greater than 83 µM) were collected using a plexiglass trap (Schindler 1969). For each sampling day, the contents of traps from 0.25, 0.75 and 1.25 meters depth were combined, dried at 60°C and weighed before radioactive analyses.

Clams (Anodonta sp.) were caged individually in epoxy-coated wire mesh cages. They were collected at the end of the experiment and frozen until dissection of the foot muscle for radioactive analyses.

All samples for ^{203}Hg and ^{75}Se analyses were contained in small petri dishes (50 mm diameter and 9 mm height) and assayed by gamma spectroscopy (Hesslein et al. 1980; Rudd et al. 1980). Five or six clams, pearl dace and crayfish from each enclosure were analyzed on each sampling date. Sample means were calculated from the log-transformed data which had been decay corrected to spike day, day zero of the experiment. Concentrations of $CH_3{}^{203}Hg^+$ in pearl dace muscle samples were determined by extraction of the $CH_3{}^{203}Hg^+$ from the samples followed by scintillation counting as described in (section 3).

Primary productivity samples were collected using a rigid PVC tube which uniformly sampled the entire depth of the water column. Productivity was assayed by the ^{14}C-incubator technique of Fee (1973a) and Shearer (1976a,b). Daily estimates of primary productivity rate were made using an empirical model under simulated cloudless conditions (Fee 1973b). These rates are probably slight overestimates of actual rates (Fee 1980).

RESULTS

Primary Productivity

Rates of primary productivity in the two control enclosures were very similar (Fig. 1) indicating that enclosure to enclosure variability was not an important factor in the interpretation of these results. Fertilization caused a large increase in the quantity of carbon fixed in the nutrient enclosures but did not affect synchrony among all of the enclosures. They had maximum photosynthetic rates early in the experiment and minimums on day 8 (Fig. 1). During the 34 day period that primary productivity was measured (day -5 to day 29) the estimated quantities of carbon fixed in the high and low nutrient enclosures exceeded the controls by ~9 times and ~4 times, respectively. These are minimum estimates of the stimulation of primary productivity because the quantities of carbon fixed between day -10, when fertilization commenced, and day -5 were not measured.

As a result of stimulating primary productivity the pH in the high nutrient enclosure increased (Fig. 2). During the experiment the mean pH in the high nutrient enclosure was 9.2 ± 0.2 ($n = 4$). The other three enclosures averaged 7.9 ± 0.25 ($n = 12$).

Dissolved and Suspended ^{203}Hg and ^{75}Se

Increasing productivity may have resulted in slightly more rapid removal of ^{203}Hg in the high nutrient enclosure (Fig. 3). Stimulating the productivity appeared to increase percentage of ^{203}Hg associated with particulate material in both nutrient enclosures (Table 2) and resulted in about 40% more ^{203}Hg-particulates being available to the food web. Most of this increase in ^{203}Hg-particulate appears to have been derived from the unassociated fraction with a lesser amount contributed by the ionic fraction.

There was no apparent effect on the loss of ^{75}Se from the water column due to nutrient addition (Fig. 3; Table 2). An average of 20% of the ^{75}Se was removed from the water column of all enclosures during the experiment. As noted previously (Hesslein et al. 1980; Rudd et al. 1980; sections 2, 3), ^{203}Hg was lost from the water column at a faster rate than the ^{75}Se. Stimulating the primary productivity also had no discernable effect on of ^{75}Se speciation (Table 2). As in the previous work (Rudd et al. 1980; section 3) more than 50% of the ^{75}Se in all of the enclosures was associated with the charcoal (organic) fraction.

Bioaccumulation of ^{203}Hg and ^{75}Se

There was excellent reproducibility of mercury and selenium bioaccumulation by pearl dace, crayfish and zooplankton between the control enclosures (Fig. 4). The range of control means usually varied by less than 10% of the combined means for all three types of organisms (Fig. 4). This suggests that enclosure to enclosure variability was not an important factor in interpreting the ^{203}Hg and ^{75}Se bioaccumulation results. Bioaccumulation trends were very similar for both mercury and selenium isotopes. Pearl dace whole body activities plateaued after 17 days of exposure; zooplankton peaked in concentration after nine days and then progressively decreased for the remainder of the experiment. Crayfish whole body activities did not reach equilibrium in either ^{203}Hg or ^{75}Se after 23 days of exposure.

Haptobenthic dry weight peaked on day 22 in all of the enclosures at 80 and 50 mg/cm^2 in the high and low nutrient enclosures respectively and at 20 mg/cm^2 in the controls. On that day ^{203}Hg activities per unit biomass in the high and low nutrient enclosures were reduced to 50% and 63%, respectively, of the combined controls. Concentrations of ^{75}Se were reduced by a smaller extent. In both the high and low nutrient enclosures, ^{75}Se activities were reduced to about 80% of the control enclosures.

Stimulation of primary productivity increased zooplankton standing crop and probably stimulated zooplankton growth. Between days 2 and 16 zooplankton dry weights in the nutrient enclosures peaked at a factor of 6 above the controls while biomass in the control enclosures remained stable. Despite the larger biomass of zooplankton in the fertilized enclosures, ^{203}Hg activities per unit mass were not substantially different (Fig. 5). Concentrations of ^{75}Se were consistently halved (Fig. 5).

After 13 days of exposure, activities of ^{203}Hg and ^{75}Se in clam foot muscle were significantly lower in the nutrient enclosures than in the controls (Table 3). Activities of both isotopes were lower in the high than in the low nutrient enclosure, suggesting dose dependent response to nutrient addition. Growth of the clams during the exposure period was not determined but in view of the faster growth observed in other test organisms, and the larger percent change in the high nutrient enclosure relative to the low nutrient enclosure (Table 3), reduced isotope concentrations may have been caused by dilution by growth.

Crayfish ^{203}Hg activities were consistently elevated in the low nutrient enclosure as compared to the controls (Fig. 6). Crayfish ^{203}Hg activities in the high nutrient enclosure were not consistently greater than in the controls (Fig. 6). Bioaccumulation of ^{75}Se was clearly enhanced in the nutrient enclosures, particularly after three weeks of exposure (Fig. 6).

The pearl dace in the fertilized enclosures grew faster in response to the enhanced primary productivity (Fig. 7a). Until the last sampling date there was no difference in body burden of ^{203}Hg between the controls and nutrient enclosures. However, after 27 days of exposure, body burdens in the high and low nutrient enclosures were 1.5 and 3 times those of the controls, respectively (Fig. 7b). In terms of ^{203}Hg activity (cpm/g) (Fig. 7c), pearl dace in the high nutrient enclosure were not different from the controls on the last sampling day; but dace from the low nutrient enclosure had twice the ^{203}Hg activity of the controls. These trends were accentuated in pearl dace muscle samples (Fig. 7d). On the last sampling day muscle ^{203}Hg activities were 4.8 and 2.7 times higher in the low and high nutrient enclosures, respectively. This last sampling point was verified by the analysis of four additional pearl dace muscle samples from each enclosure.

Pearl dace ^{75}Se body burdens in the nutrient enclosures were reduced to about 75% of the controls (Fig. 7b). Whole body ^{75}Se activities (cpm/g) were reduced to about 60% of the controls independent of nutrient loading (Fig. 7c). Activites of ^{75}Se in pearl dace muscle samples were reduced by approximately the same extent as the whole body activities (Fig. 7d).

DISCUSSION

Effects of Primary Productivity on Mercury Bioaccumulation

The four and nine fold increases in primary productivity of the nutrient enclosures (Fig. 1) appeared to affect two factors known to influence fish mercury concentration: growth rate, and rate of supply of methyl mercury to the fish. Fish growth rate responded according to the fertilization rate with pearl dace in the high nutrient enclosure growing faster than dace in the low nutrient enclosure (Fig. 7a). Mercury methylation rates in the nutrient enclosures were probably also stimulated by the increased rate of supply of algal fixed carbon. Rapid increases in methylation rate have been found after addition of bacterial organic carbon substrate to Clay Lake water and sediment samples (section 6) and by the addition of undecomposed sphagnum moss to an enclosure at Southern Indian Lake (Hecky et al. unpub data). In our experiment there appeared to be a increase in rate of supply of methyl mercury towards the end of the experiment, when pearl dace ^{203}Hg body burden increased rapidly (Fig. 7b). This was more noticeable in the dace muscle samples which had large increases in ^{203}Hg activity on the last sampling data (Fig. 7d). This total ^{203}Hg was found to be 77% ± 8 and 83 ± 3% $CH_3{}^{203}Hg^+$ in the low and high nutrient enclosures respectively, suggesting that there was more $CH_3{}^{203}Hg^+$ available for bioaccumulation in these enclosures. The much lower muscle mercury concentration in the control enclosure (Fig. 7d) was found to be composed of only 60% $CH_3{}^{203}Hg^+$. This lower percentage of $CH_3{}^{203}Hg^+$ also suggests a lower methylation rate in the unfertilized control enclosures.

In the high nutrient enclosure, the enhanced fish growth rate offset the increased body burden of ^{203}Hg such that there was no increase in ^{203}Hg activity (cpm/g) of the pearl dace (Fig. 7c). In the low nutrient enclosure, however, the much larger increase in ^{203}Hg body burden was not offset by growth. In this case, fish ^{203}Hg activities were twice control values at the end of the experiment (Fig. 7c). A similar observation was made for the crayfish (Fig. 6).

Even though there was more than twice as much newly fixed carbon (bacterial substrate) in the high nutrient enclosure as compared to the low nutrient enclosure, fish and crayfish mercury concentrations were lower in the high nutrient than in the low nutrient enclosure (Figs. 6, 7b, c, d). A possible explanation is the 40 fold difference in hydrogen ion concentration between the enclosures (Fig. 2) resulting from the higher photosynthetic rates in the high nutrient enclosure (Fig. 1). A change in pH may affect the efficiency with which fish bioaccumulate mercury (Drummond et al. 1974). In addition, increasing pH above prevailing values has been found to substantially reduce the rate of methyl mercury production by natural populations of sediment bacteria (Rudd unpublished data). And, high pH may also favor the the formation of dimethyl mercury which is more volatile than methyl mercury and may be lost to the atmosphere rather than bioaccumulated (Jernelov et al. 1975; 1976).

The overall effects of increasing primary productivity on fish mercury concentration appear to be a complex interrelationship of stimulation of fish growth rate and microbial methylation rate plus, in some cases, a change in pH which may reduce either fish bioaccumulation efficiency of CH_3Hg^+ or change the form of methylated mercury produced by micro-organisms. Increases in primary productivity that were not large enough to affect ecosystem pH produced the largest increases in mercury concentration of the pearl dace and crayfish (Fig. 7c, d). This set of circumstances appears to be optimal for mercury methylation and bioaccumulation.

Although elevated pH inhibited mercury bioaccumulation somewhat (Fig. 7b, c, d at high vs low nutrient enclosures) as predicted by other researchers (Jernelov, 1975; 1976; Beijer and Jernelov et al. 1979), increasing productivity, pH, and fish growth did not result in the predicted decrease in fish mercury concentration as compared to the controls (Fig. 7c;Jernelov 1975, 1976; Beijer and Jernelov 1979). In our case this was probably because there was a small increase in mercury methylating activity at high pH. This may have nullified the effect of dilution by increased fish growth rate (Fig. 7a and c).

The haptobenthos and the clams were the only members of the food web that consistently decreased in mercury activity as a result of stimulating the primary productivity (Table 4). This may have been caused by faster growth rates in the nutrient enclosures (2.4 - 4.0 times for haptobenthos) together with their usual inefficiency in mercury bioaccumulation as compared with higher members of the food chain (Huckabee et al. 1979; Smith et al. 1975). Mercury bioaccumulation by zooplankton and pearl dace either eventually kept pace with or exceeded dilution due to enhanced growth rates (Fig. 5, 7a-d). A similar trend was also found for the crayfish although growth could not be estimated in this case (Fig. 6).

Increasing primary productivity by addition of algal nutrients has been suggested as a mercury ameliorating technique. Our experimental results suggest that this could be unsuccessful. Instead this treatment would probably result in stable or increased fish mercury concentration depending on presence or absence and size of pH changes following nutrient addition. By extension, our results suggest that lowering primary productivity by reducing nutrient input would lower methylation rates. However, this treatment would probably also reduce fish growth rates so that the long term effect on fish mercury concentrations would be difficult to predict.

Effects of primary productivity rate on selenium bioaccumulation

Stimulating ecosystem primary productivity by nutrient addition resulted in a decrease of about 50% in the ^{75}Se activities of the haptobenthos, zooplankton, clams and pearl dace in the nutrient enclosures relative to the controls (Figs. 5, 7, Table 3). This was probably due to dilution of ^{75}Se by enhanced growth rates of the food chain organism in the nutrient enclosures (Fig. 1, 7a). The only exceptions were the crayfish which had lower ^{75}Se activities in the controls than in the nutrient enclosures (Fig. 6). The crayfish also had much lower absolute ^{75}Se concentration (cpm/g) than the zooplankton or pearl dace (Fig. 4). This was not surprising because the crayfish were caged and fed unlabelled white sucker flesh. At the trace selenium levels present in this experiment (≈0.2 μg Se/L), selenium is predominantly bioaccumulated through the food chain (Rudd et al. 1980, sections 3,4). Thus, this difference between control and nutrient enclosures crayfish was probably an effect in the selenium bioaccumulation from water, which is a minor source.

The general decrease in ^{75}Se activities of the biota in the nutrient enclosures suggets that bioaccumulation of selenium to toxic levels is not as likely in productive systems than in less productive systems. The oppositeresponse of rates of mercury-203 and selenium-75 bioaccumulation to enhanced primary productivity would tend to increase the Hg:Se ratio in fish flesh. Because of the known antidotal effect of selenium on mercury (Friedman et al. 1978; Ohi et al. 1976; Ganther and Sunde 1979; Frost and Lish 1975), stimulation of primary productivity might increase the toxicity of methyl mercury to the fish consumer.

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Table 1. Chronology of enclosure additions.

Days After Isotope Addition	Addition
-12 to -10	Enclosures filled
-10	3 kg NaCl per enclosure Low nutrient enclosure: 7.12 g NaH_2PO_4 and 127 g $NaNO_3$ High nutrient enclosure: 18.04 g NaH_2PO_4 and 314 g $NaNO_3$
-5	Begin weekly additions of: Low nutrient: 3.6 g NaH_2PO_4 and 63 g $NaNO_3$ High nutrient: 9.02 g NaH_2PO_4 and 157 g $NaNO_3$
0	$^{203}Hg(NO_3)_2$ and $^{75}SeO_3^{=}$ to each enclosure on June 4, 1979
4	60 pearl dace per enclosure at 40 kg/ha
7	18 crayfish per enclosure
9	6 clams per enclosure
30	Termination of experiment

Table 2. Partitioning of ^{203}Hg and ^{75}Se in four water samples taken from control and nutrient enclosures during a 30 day experiment.

Enclosure	% Particulate	% Charcoal	% Ionic	% Unassociated
		^{203}Hg		
C_1	27.4 (±8.1)	24.9 (±8.3)	14.5 (±5.3)	33.1 (±15.3)
C_2	26.5 (±4.7)	24.6 (±7.5)	13.4 (±4.8)	35.4 (±11.3)
Low nutrient	36.0 (±10.0)	23.3 (±4.9)	12.2 (±4.7)	28.5 (±10.4)
High nutrient	38.8 (±5.5)	26.0 (±5.6)	11.9 (±2.0)	23.3 (±5.5)
		^{75}Se		
C_1	23.2 (±16.9)	51.1 (±12.3)	25.7 (±11.5)	-
C_2	25.0 (±19.6)	53.4 (±16.9)	21.6 (±9.8)	-
Low nutrient	23.6 (±17.1)	53.3 (±13.2)	23.1 (±8.5)	-
High nutrient	23.9 (±19.0)	55.0 (±14.4)	21.1 (±7.5)	-

Table 3. Bioaccumulation of ^{203}Hg and ^{75}Se in the foot muscle of clams held in enclosures of varying primary productivity. Log-normal means of five clams are presented for the nutrient enclosures and ten clams for the combined controls.

Treatment	^{203}Hg (cpm/g $\overset{\div}{\times}$ SD)	^{203}Hg as % of controls	^{75}Se (cpm/g $\overset{\div}{\times}$ SD)	^{75}Se as % of controls
Combined controls	265 ($\overset{\div}{\times}$ 1.28)	100	190 ($\overset{\div}{\times}$ 1.48)	100
Low nutrient	192 ($\overset{\div}{\times}$ 1.21)	73	92 ($\overset{\div}{\times}$ 1.30)	48
High nutrient	141 ($\overset{\div}{\times}$ 1.55)	53	64 ($\overset{\div}{\times}$ 1.45)	34

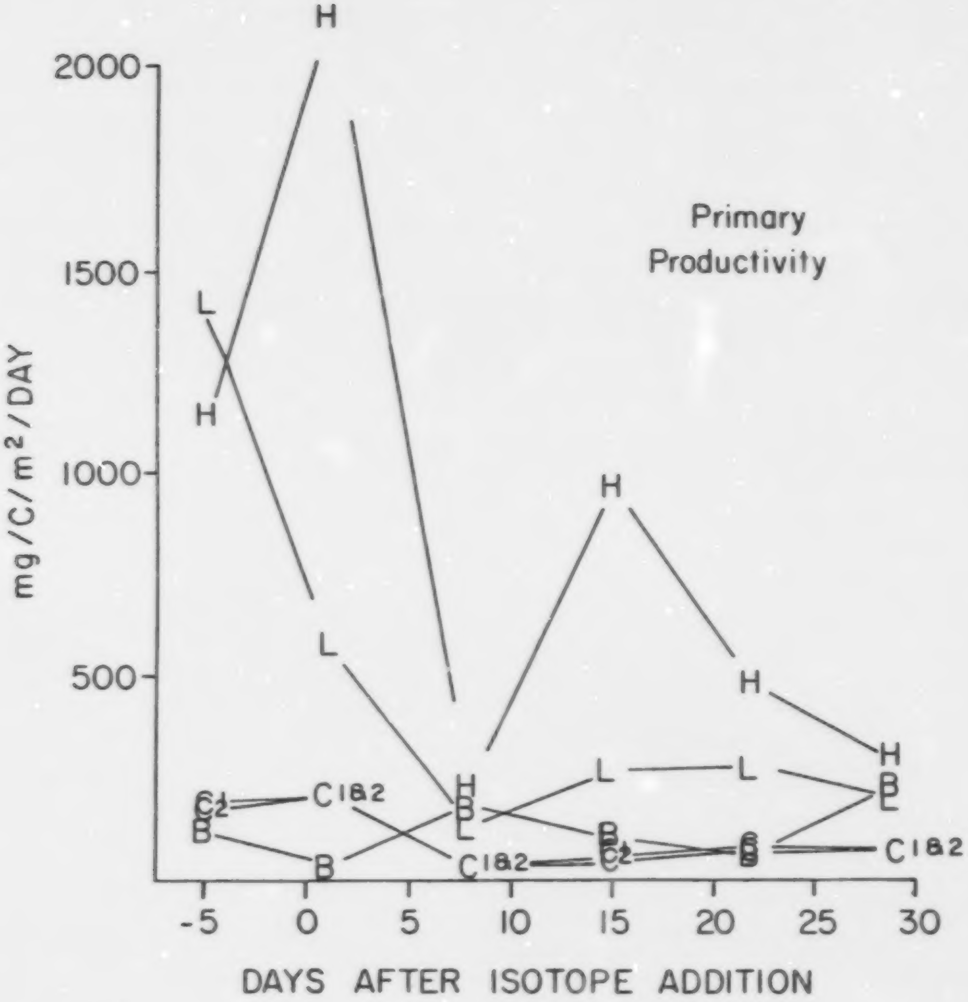

Fig. 1. Daily rates of primary production under cloudless conditions in the control (C1 and C2), low nutrient (L), and high nutrient enclosures (H) and in Clay Lake outside of the enclosures (B).

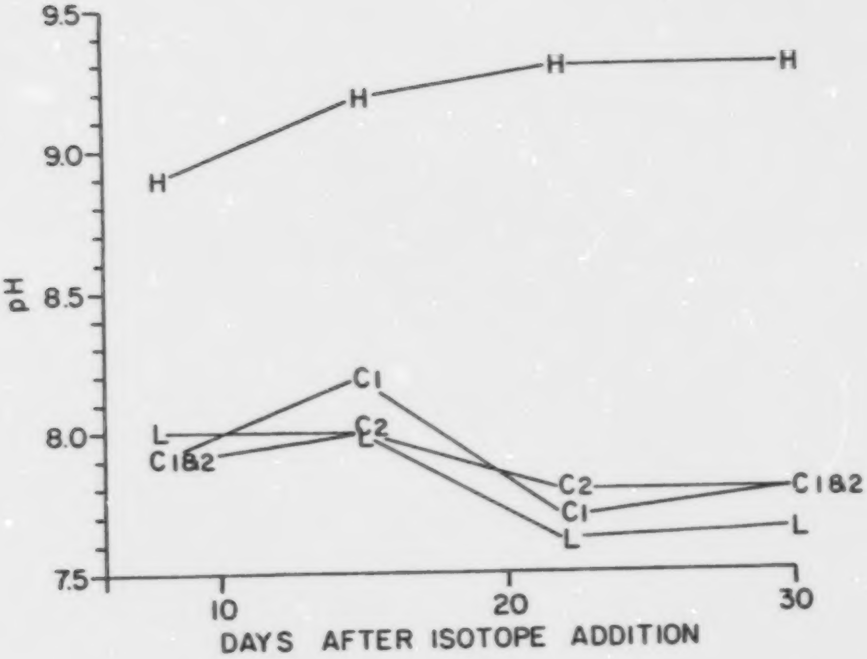

Fig. 2. pH of water samples taken from the high nutrient (H) low nutrient (L) and control enclosures (C1 and C2).

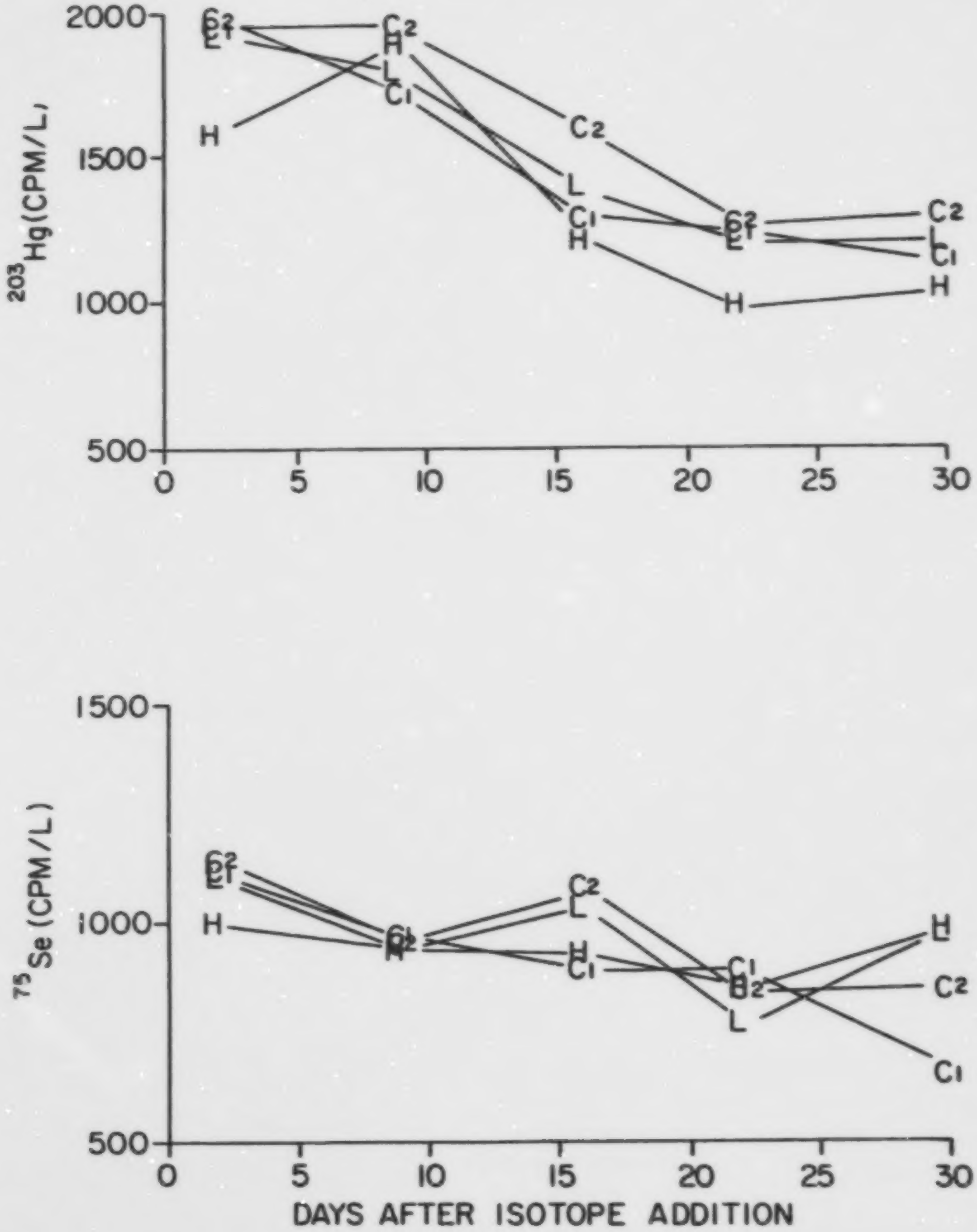

Fig. 3. Total concentrations of ^{203}Hg and ^{75}Se from the water columns of the control (C1 and C2), low nutrient (L) and high nutrient (H) enclosures as a function of time. Isotope activities are the sums of all of the mercury and selenium species.

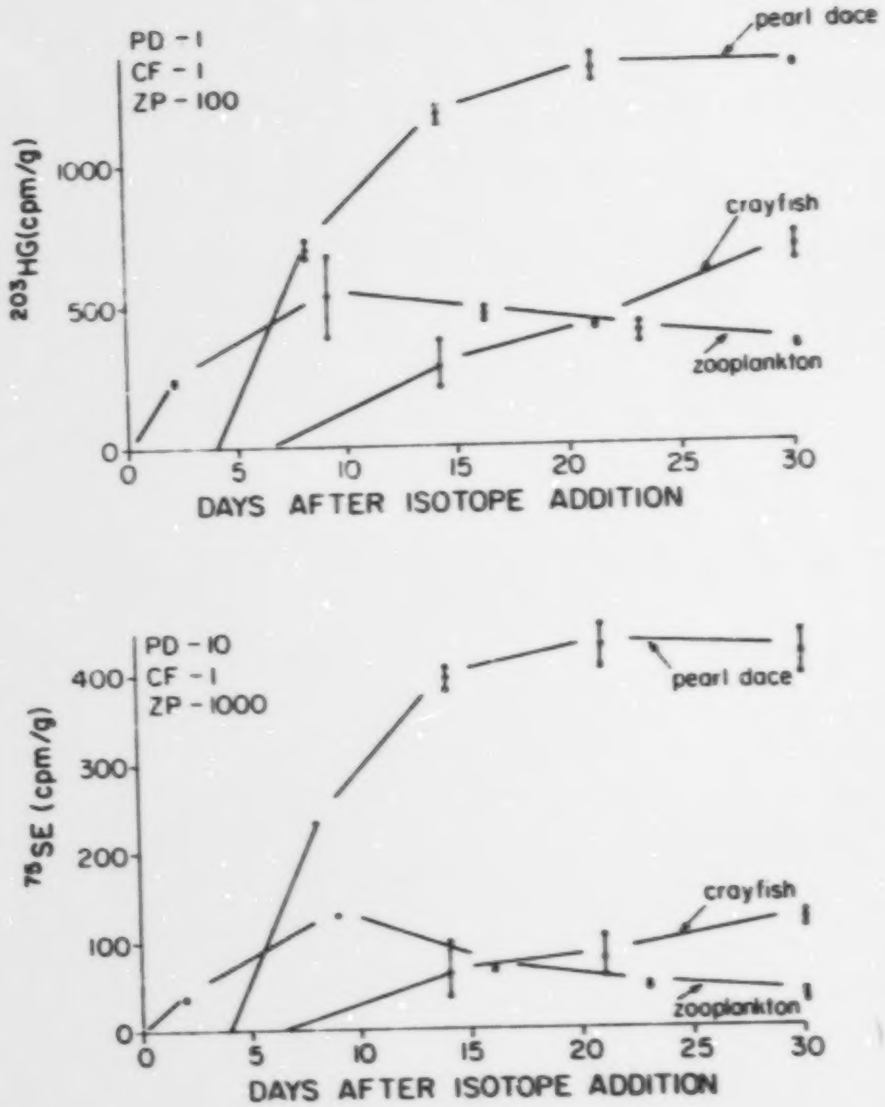

Fig. 4. Time course estimates of ^{203}Hg and ^{75}Se concentrations in a pearl dace and crayfish whole bodies and in zooplankton samples taken from the control enclosures. The vertical lines connect the lognormal means of concentrations in the two control enclosures.

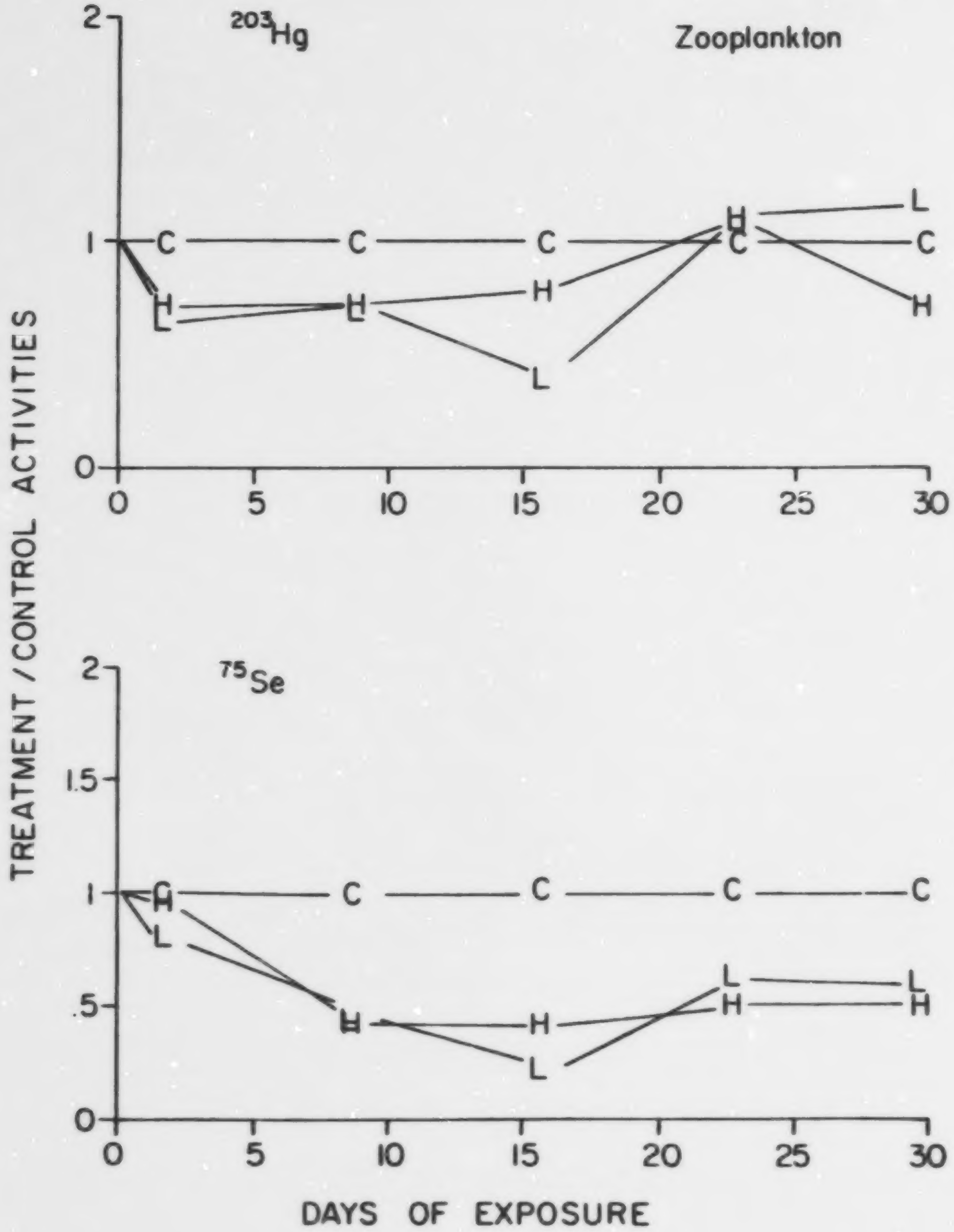

Fig. 5. Ratios of ^{203}Hg and ^{75}Se activities of zooplankton samples taken from the high (H) and low (L) nutrient enclosures and from the controls. The ratios were calculated by dividing activities of the samples from the nutrient enclosure by samples from the control enclosures.

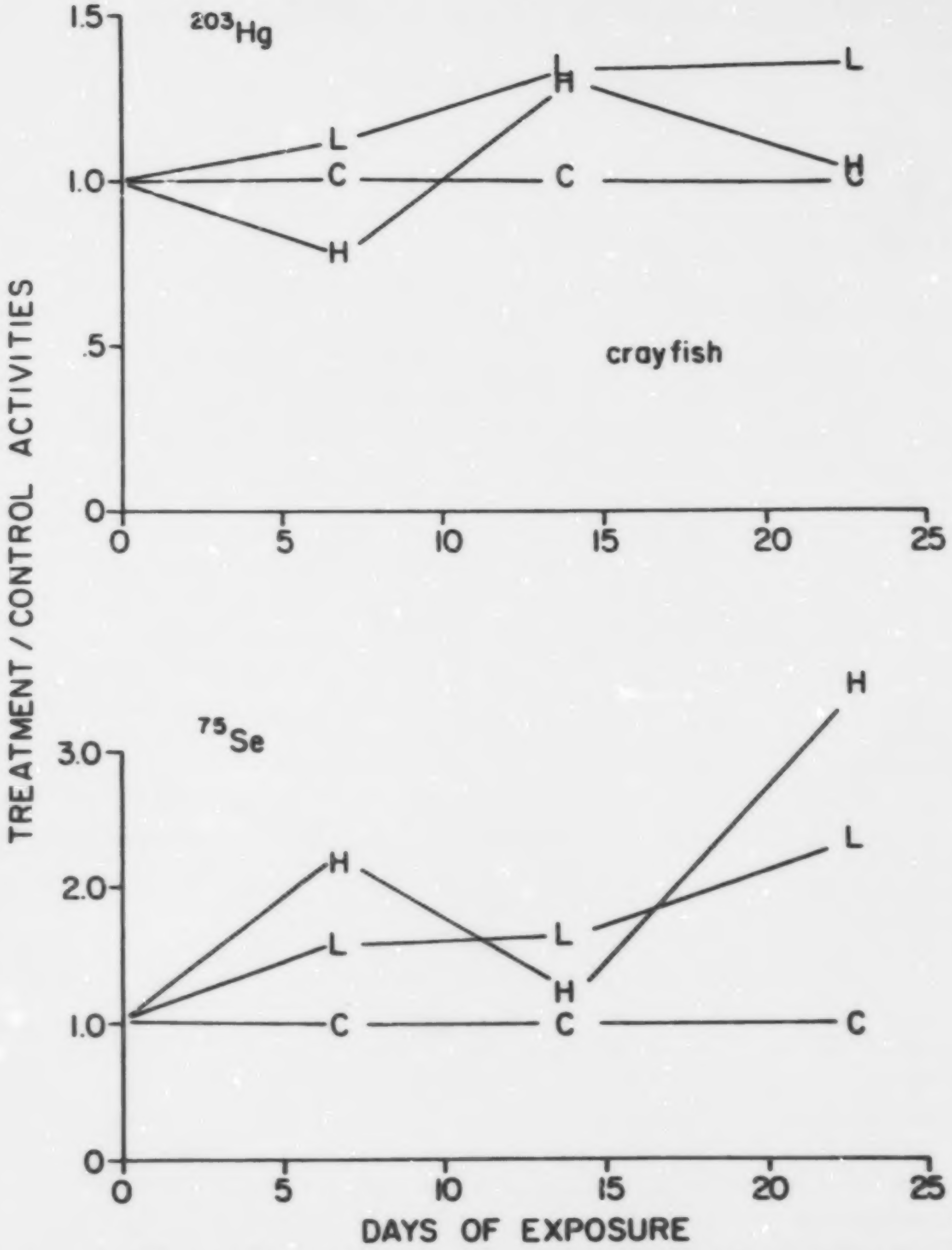

Fig. 6. Ratios of ^{203}Hg and ^{75}Se activities in whole body crayfish samples taken from the high (H) and low (L) nutrient enclosures and from the controls (C). The ratios were calculated by dividing activities of of the samples from the nutrient enclosures by samples from the control enclosures.

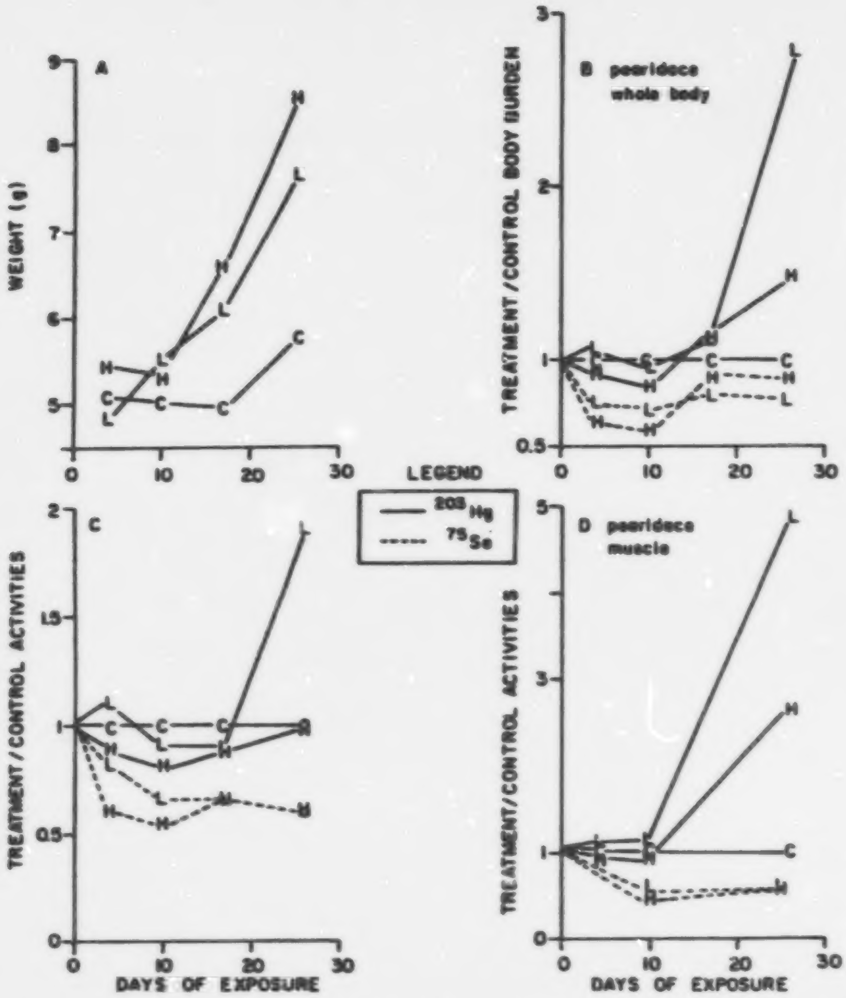

Fig. 7A. Lognormal mean weights of pearl dace taken from the control (C), high (H) and low (L) nutrient enclosures.

7B. Ratios of ^{203}Hg and ^{75}Se body burdens of pearl dace taken from the high (H) and low (L) nutrient enclosures to the controls (C). The ratios were calculated by dividing activities of samples from the nutrient enclosures by activities of samples from the control enclosures. Solid and broken lines represent ^{203}Hg and ^{75}Se respectively.

7C. Ratios of ^{203}Hg and ^{75}Se activities of pearl dace whole body samples from the high (H) and low (L) nutrient enclosures to the controls (C). The ratios were calculated by dividing activities of samples from the nutrient enclosures by activities of samples from the control enclosures. Solid and broken lines represent ^{203}Hg and ^{75}Se respectively.

7D. Ratios of ^{203}Hg and ^{75}Se activities of pearl dace skeletal muscle samples from the high (H) and low (L) nutrient enclosures to the control enclosures (C). The ratios were calculated by dividing activities of samples from the nutrient enclosures by activities of samples from the control enclosures. Solid and broken lines represent ^{203}Hg and ^{75}Se respectively.

6. MEASUREMENT OF MERCURY METHYLATION IN LAKE WATER AND SEDIMENT SAMPLES

Akira Furutani and John W.M. Rudd

ABSTRACT

Biological mercury methylation was assayed by a new radiochemical technique in the water column and sediments of a mercury-contaminated lake. In 24 weeks during 1979, there were three episodes of methylating activity in surface floc and in water, each lasting 3 to 5 weeks. Periods of methylation in the water column coincided with surface sediment methylation and appeared to be related to overall microbial activity. Mercury was actively methylated in the presence of bound sulfide.

INTRODUCTION

Sites of biological mercury methylation in contaminated lakes have been of interest for a number of years. Most studies have concluded that methylation occurred in the sediment (2, 22, 25, 29).

One of the major limitations of methylation studies has been the low sensitivity of the methodology to measure in situ methylmercury production (8, 34). Long incubation times of several weeks, increased mercury concentrations, or both have been necessary to detect methylation (15, 20, 23, 28). These conditions have an unknown effect on the natural microbial community and limit the usefulness of this approach as an indicator of in situ mercury methylation.

As an alternative to the direct measurement of methylation rates in the sediments, live fish have been utilized as bioaccumulators of methylmercury (16, 23, 27). However, this indirect laboratory method also requires long incubation times and provides limited information on the in situ activities of methylating bacteria. In addition, other methylation sites such as the water column, fish intestinal contents and slime, and other intermediate steps of the food chain cannot be investigated individually (24, 31).

This paper presents methylmercury production data obtained by using a very sensitive radiochemical technique on natural lake samples. The samples were taken from Clay Lake, Ontario, which has been severely contaminated with mercury for the past 17 years (3). Methylation in the water column, in the layer of recently deposited organic floc at the sediment-water interface, and in the gastrointestinal tract of several fish species has been investigated. Methylation data for the first two sites are described in this paper. The intestinal methylation data are presented by Rudd et al. in the following article (31).

MATERIALS AND METHODS

Sampling. Samples were collected fom the unstratified eastern and the stratified western basins of Clay Lake (Z_{max}, 3 and 18 m, respectively). Water samples from the aerobic eastern basin were taken approximately 10 cm below the surface by submerging an 8-liter polyethylene bottle. From the deeper western basin, depth profile samples for methylating activity were taken by a Van Dorn sampler and transferred into three heat-sterilized 270-ml reagent bottles for each depth sampled. These bottles were overflowed to minimize atmospheric oxygen contamination.

Much of Clay Lake has a heavy gray-colored clay bottom with a thin overlying layer of recently deposited organic-rich flocculent material, which is brown in the eastern basin but black in the deeper, anoxic western basin. This organic-rich layer (sediment-floc) was collected by an Ekman grab, which sampled 233 cm^2 of surface area (11). For the samples from the aerobic eastern basin, the Ekman grab was rocked until the sediment-floc was suspended in the overlying water. The suspension was then transferred with a 50-ml syringe to a 1-liter plastic bottle. For the anoxic western basin samples, the floc was withdrawn through the undisturbed overlying water with a syringe and transferred into a glass reagent bottle until completely filled. This procedure minimized exposure to atmospheric oxygen.

Methylation incubation. This method used a bottle incubation of environmental samples in the presence of $^{203}Hg(NO_3)_2$ (1 mCi/mg, New England Nuclear Corp.). More than 95% of the ^{203}Hg was immediately adsorbed by the particulate matter in the samples. After incubation, radioactive methylmercury produced during the incubation period was extracted using a modified solvent extraction technique and assayed by scintillation spectrometry. All methylation incubations were in preignited (450°C) 270-ml glass reagent bottles. Each test used three incubation bottles: duplicate tests and a control. The control samples were fixed before incubation by 1 ml of 4 N HCl. Incubation was started within 2 h of samplng. The test samples were acidified to terminate incubation. The incubation period was 4 days at in situ temperatures in the dark. Water samples from the anoxic hypolimnion were directly spiked with 0.41 µCi of ^{203}Hg, an equivalent concentration of ^{203}Hg.

The sediment-floc samples from the eastern basin were transferred in 100-ml portions into the incubation bottles and spiked with 0.3 µCi of ^{203}Hg. The 270-ml samples of anaerobic hypolimnetic sediment-floc were directly spiked with 0.80 µCi of ^{203}Hg (an equivalent ^{203}Hg concentration).

[^{203}Hg]methylmercury extraction. After acidifying the samples, the $CH_3{}^{203}Hg^+$ could be stored for up to 5 days before extraction without loss of activity. The solvent extraction method developed by Utne et al. (37), intended to extract methylmercury from fish tissues, was modified to extract radioactive methyl-mercury produced during incubation of sediment-floc and water column samples. A 2-ml volume of 0.5 M copper sulfate and 10 ml of 3 M sodium bromide in 11% sulfuric acid were added to the samples. After mixing and standing, the water column samples and the supernatant of the "settled" sediment-floc samples (usually 60 to 80 ml) were transferred into 125-ml glass separatory funnels. A 20-ml volume of glass-distilled toluene (Caledon) was added and shaken for at least 3 min. The aqueous phase was removed, and the remaining toluene phase was dried with about 1 g of anhydrous sodium sulfate. The toluene phase was decanted into a 50-ml Erlenmeyer flask and further dried with about 0.5 g of sodium sulfate. A 10-ml sample of the dried extract was placed in a clean separatory funnel, to which 5 ml of 0.0025 M sodium thiosulfate in 20% ethanol was added.

Then 3 ml of the lower aqueous phase was pipetted into a glass-stoppered test tube to which 1 ml of 3 M potassium iodide and 1 ml of glass-distilled benzene (Caledon) were added. Subsamples (250 µl) of the extracted monomethylmercury iodide concentrated in the benzene phase were assayed for radioactivity by liquid scintillation counting in 10 ml of PCS cocktail (Amersham) and, if required, for total methylmercury concentration by gas chromatography using an electron capture detector (37). The extraction efficiency was 97 to 100%. The scintillation counting efficiency was 85% based on comparison with a gamma counter of a known efficiency.

Extraction confirmation. Benzene extracts were analyzed for organic ^{203}Hg before and after addition of equal volumes of saturated silver sulfate to bring organic ^{203}Hg into the aqueous phase (21).

For specific identification and confirmation of $CH_3{}^{203}Hg^+$ production, two different thin-layer chromatography systems were used. The first system used was Baker-flex silica gel IB-F 4463 plates (Machrey and Nagel Polygrams) with ethyl ether-petroleum ether (3:7) as the solvent. The second system used silica gel plates (Kodak 13179 with 6061 fluorescent indicator) with hexane-acetone (9:1) as the solvent (36). The extracted radiomercury in the benzene was supplemented with cold monomethylmercury iodide, which permitted visualization with 0.05% dithiazone in chloroform. After partioning, 1-cm-interval scrapings of the silica gel were assayed by scintillation counting and were compared with the R_f value of a simultaneously run cold monomethylmercury iodide control.

The method was also tested to confirm that non-biological isotopic exchange was not responsible for $CH_3{}^{203}Hg^+$ production. Samples of lakewater were treated as described in Table 1. The methylmercury was filter sterilized, and the $^{203}Hg^{2+}$ was sterilized and rendered free of organic matter by photooxidation (6). The autoclaved samples were completely cooled before the sterilized spikes were introduced, to avoid isotopic exchange induced by high temperature (18). Bacterial growth was measured turbidimetrically on day 4 of incubation. The above described incubation, extraction, and measurement procedures for radioactive methylmercury were used.

Other analyses. Samples for methylmercury and total mercury concentrations as well as for oxygen depth profiles were obtained by the same methods as used in methylmercury production sampling. Methylmercury samples were preserved with sulfuric acid at 0.3% final concentration and transported in 8-liter polyethylene bottles. Dissolved methylmercury was extracted using the 5-liter continuous extractor method of Chau and Saitoh (12) and analyzed by gas chromatography. Total mercury samples, preserved with final concentrations of 0.05% chromate and 1% nitric acid, were transported in preignited glass reagent bottles. Total mercury was determined by flameless atomic absorption spectrometry (A. Lutz, manuscript in preparation). Sediment-floc samples dried at 60°C were assayed for total mercury (5) and for organic carbon (33).

Dissolved oxygen profiles were assayed according to the Hach analytical method. Biological oxygen demand measurements were conducted on 40-ml epilimnetic samples contained in

50-ml glass syringes. Four replicates were analyzed after 0, 6, 12 and 24 h of incubation by the semi-micro method of Rudd et al. (3).

RESULTS

Confirmation of $CH_3\,^{203}Hg^+$ production. On every occasion (11 times) when silver sulfate was added to the benzene extract, the methylmercury peaks on the chromatograms and the radioactive counts disappeared. This indicated that the radioactivity was in an organic mercury compound.

More than 90% of the radioactivity in the thin-layer chromatograms was found in the same area as the monomethylmercury iodide control. The R_f values were 0.55 for the Kodak system and 0.4 for the Bakerflex system.

The results of bacterial growth and isotopic exchange experiment are shown in Table 1. At concentrations up to 0.1 μg of methylmercury per ml, no significant isotopic exchange occurred under these conditions in the sterilized controls. Acidification of samples provided a satisfactory control since it effectively stopped bacterial growth and mercury methylation, and it did not enhance isotopic exchange. The amount of methylation (disintegrations per minute) paralleled the amount of bacterial growth (optical density) in this test.

Jacobs and Keeney (20) found it necessary to test for recovery of methylmercury with different sediment types. Three methylmercury recovery tests were conducted on sediment-floc of the eastern basin during the year. A 10-ng sample of methylmercury was added to 100 ml of sediment-floc suspension (~1.5 g, dry weight). In each case, all of the methylmercury was recovered (95 to 103%).

Eastern basin. Samples of the sediment-floc from the eastern basin were tested during the summer of 1979 to determine whether methylation occurred and, if so, to obtain some impression of the variation of methylating activity with time. Averages of duplicate analyses of sediment-floc samples are presented in Fig. 1. Mean percent coefficient of variation for these samples was 9.9 ± 10.2% for 14 duplicates. Methylating activity occurred in three separate peaks. The first and largest peak coincided with the spring run-off, when the water residence time in Clay Lake was reduced from about 50 to 10 days.

Mercury methylation also occurred in the water column (Table 2 and Fig. 1). The peaks of activity in the water column samples coincided with the peaks of activity of the sediment-floc samples.

On 10 July 1979, lake water and sediment-floc samples were enriched with 2 mg of tryptic soy broth (Difco) per ml to determine whether the methylating process was limited by bacterial substrate. Tryptic soy broth contains organic carbon, energy, and nutrient sources which are easily utilized by a wide variety of bacterial species. The methylating activity of the water column samples increased 15 times, and that of the sediment-floc samples increased 315 times (Table 2).

On four occasions the role of bacterial substrate was further investigated in the water column samples by monitoring the biological oxygen demand over a 24-h period. In Fig. 2

the methylating activity of the water column samples is plotted against the rate of oxygen consumption. These data suggest a linear relationship between overall microbial activity (i.e., community respiration) and the rate of methylation. Total mercury concentrations of these water samples were found to be unrelated to changes in methylating activity (Table 2). Similar oxygen demand measurements were attempted on sediment-floc samples, but rapid chemical uptake of oxygen masked the biological oxygen consumption. In this case methylation was found to be not correlated with the organic carbon content of the sediments samples (Table 2). This may have been because the organic carbon was not readily available as a bacterial substrate.

Western basin. During the summer of 1979, 1-m epilimnion and composite hypolimnion mercury methylation samples were taken from the stratified western basin. After August, no methylation in the water samples was detected (Table 2), although hypolimnetic methylmercury concentrations increased (Fig. 3; a similar increase was noted in 1978 by J.W. Parks [personal communication]). The hypolimnetic sediment-floc at this site was, however, actively methylating (Table 2). Thus increased methylmercury concentrations probably resulted from diffusion away from the sediment-floc.

Late in the summer the sediment-floc of the anoxic portion of the hypolimnion of the western basin was black. When these samples were acidified, the black color rapidly changed to the same brown color of the eastern basin and there was a strong hydrogen sulfide odor, indicating that the sulfide was bound as insoluble iron sulfide. Despite the presence of sulfide, which is known to tightly bind mercury (K_{sp}, 10^{-53}), $^{203}Hg^{2+}$ was actively methylated on each occasion (Table 2).

DISCUSSION

The production of $CH_3{}^{203}Hg^+$ frm inorganic $^{203}Hg^{2+}$ was confirmed by the silver sulfate test and by the two thin-layer chromatography methods. It was concluded that chemical isotopic exchange was not interfering with the measurement of biological methylation (Table 1); this agrees with Kudo et al. (26), who found insignificant isotopic exchange under expected environmental conditions. We conclude that biological mercury methylation was being assayed by the technique described.

There are several advantages and some limitations in using this radioactive technique. Use of the isotope allowed mercury methylation to be detected with much greater sensitivity than the chemical methods. The incubation period could be reduced from weeks to 4 days, enabling the detection of short-term fluctuations in in situ activity. It also decreased the effects of enclosing a microbial community in a bottle. There is evidence (24a) that surface sediments from Frain's Lake, Michigan, could be incubated in the laboratory for at least 4 days without changing the overall microbial activity of the sediments.

Another advantage of this technique is that because only a small amount of mercury is added to the samples, in comparison to previous incubation techniques with stable mercury, the selection of a more mercury-tolerant bacteria would probably be minimized (38). This increases the likelihood that the methylating activity observed was from the same microbial population that was active in the lake sediment and water at the time the samples were collected. The amount of mercury added in our technique was the carrier mercury of ^{203}Hg used for the spikes, about 0.3 to 0.6 μg of Hg per spike.

A limitation of the method is that it is not a conventional radiotracer method. A tracer method requires that the mercury isotope be in equilibrium with all mercury species in the sample (9). In these experiments, free $^{203}Hg^{2+}$ was added to samples containing mercury naturally complexed to clays and organic materials, and isotopic equilibrium was probably not achieved during the incubation period. It is also necessary to know the concentration of the bioavailable mercury species, which we were not able to measure. Therefore, absolute methylation rates, i.e., micromolar per liter per hour, cannot be calculated. Although the quantity of free carrier mercury added to the samples was small, the total mercury concentrations in the water samples were increased about 300-fold. For sediment-floc samples the total mercury concentrations were increased only about a tenth, but the in situ bioavailable mercury was probably increased significantly, since, in experiments using mild mercury extraction techniques, i.e., calcium chloride, extractable mercury was less than 0.01% of the total mercury in Clay Lake sediments (19). Thus if the in situ bioavailable mercury pool was significantly increased with labeled Hg^{2+}, and because mercuric ion is the mercury species that is the substrate for biological methylation (7, 14), then methylation rates could be expressed as a relative rate (i.e., disintegrations per minute per liter per hour). This appears to be a valid approach since we have observed progressively increasing disintegrations per minute (radioactive methylmercury) concentration in time course experiments in the laboratory (Table 1) and in field samples (31).

Although methylating activity can be compared within the same compartment of a lake, comparison between compartments (e.g., water versus sediments) may not be meaningful because of the large differences in mercury concentrations. Differences in ability of sediment type to complex mercury should also be considered. For example, production of $CH_3{}^{203}Hg^{+}$ by sediment-floc of non-mercury-contaminated Lake 114 in the Experimental Lakes Area (10) was about 10 times more rapid than that in mercury-contaminated Clay Lake. The most obvious differences between these sediments were the lower mercury concentration and smaller quantities of clay in Lake 114 sediments.

Despite its limitations, the method can be successfully applied to a wide variety of environmental research problems. These data are the first reported for biological mercury methylation in the water column of a lake (Fig. 1, Table 2), a possible significant source because of the lake's large volume. Armstrong and Scott (4) suggested, when evaluating mercury concentration changes in sediment, water, and fish, that biological mercury methylation might occur in Ball Lake, which is downstream in the same polluted system as Clay Lake, and Rudd et al. (32), in limnocorral experiments, concluded that it probably occurred in Clay Lake. Photochemical mercury methylation at the lake surface is another possibility, although this has only been demonstrated in the laboratory (1).

Coincident peaks of cyclic methylation activity in the sediment-floc and the water column of the eastern basin (Fig. 1, Table 2) suggest that there was a common factor controlling methylation. It is not known whether the cause of this cyclic behavior is the same as that noted by Hamdy and Noyes (17) when they investigated methylation by pure bacterial batch cultures. In Clay Lake, it appears from experiments on nutrient addition (Table 2) and community oxygen consumption (Fig. 2) that nutrient supply and microbial activity are the important factors controlling in situ methylation (23, 27). If this is the case, then the cyclic nature of methylation could be caused by the cyclic supply of phytoplankton-derived bacterial substrates (34) or periodic resuspension of sediments.

It is generally conceded that mercury methylation is reduced by about 10^{-3} in the presence of sulfide (15, 20) because Hg^{2+} is precipitated ($K_{sp} = 10^{-53}$) as bio-unavailable HgS. Jacobs and Keeney (20) accounted for the observed slow methylation in the presence of sulfide by suggesting that complexing organics competed with the sulfide to provide bioavailable organically complexed Hg^{2+}.

In Clay Lake the $^{203}Hg^{2+}$ was actively methylated in sulfide-containing sediment-floc samples taken from the anoxic western basin. Jackson and Woychuk (19) in their study of the same basin in 1978 found sediment pH of 6.6 with about 30 μg (dry weight) of bound sulfide per g. The sulfide was present as amorphous FeS (G.J. Brunskill, personal communication), which has a dissociation constant of about 10^{-16} to 10^{-17} (13). Probably the geochemical dissociation of FeS and the sulfide binding of mercuric ion as HgS did not occur quickly enough to severely inhibit methylation, since the activity of the anoxic western basin samples and that of the aerobic eastern basin sediment-floc samples were not dissimilar (Table 2).

This observation may have important consequences for the mercury methylation process and movement of mercury through aquatic ecosystems. In the case of the western basin of Clay Lake, some of the mercury entering the anoxic sediments on particulates was probably methylated before it could be bound as mercury sulfide. The result was the gradual accumulation of hypolimnetic methylmercuy in the presence of sulfide as shown in Fig. 3. Thus, instead of being permanently sequestered in the sediments as HgS, some of the newly sedimented mercury was released back into the lake water as methylmercury.

ACKNOWLEDGEMENTS

The encouragement and valuable advice received from F.P. Healey and F.A.J. Armstrong throughout the developmental to the manuscript stages is very much appreciated. C. Tam and M.P. Stainton provided their expertise in the development of the method. A. Lutz and his staff kindly analyzed the total and methylmercury samples. We are thankful for the assistance of B.E. Townsend for field sampling and of E. Slavicek for the numerous extractions. The helpful comments on the manuscript by J.F. Klaverkamp, R.D. Hamilton, and M.A. Turner are gratefully acknowledged.

This work was supported by the Department of Fisheries and Oceans and through the Canada Water Act by the Inland Water Directorate and by the Government of Ontario.

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Table 1. Test for non-biological isotopic exchange[a]

Sample treatment	dpm/ml on day of incubation: 0	1	4	Optical density[b] (day 4)
No MeHg[c] added	0	0	207	0.260
Autoclaved	0	0	7	0.025
MeHg (0.01 µg/ml)	0	5	304	0.290
Autoclaved	0	1	5	0.016
MeHg (0.02 µg/ml)	0	0	18	0.130
Autoclaved	0	6	2	0.018
MeHg (0.10 µg/ml)	0	5	96	0.220
Autoclaved	0	3	9	0.018
MeHg (0.02 µg/ml) + HCl	0	0	0	0.016
Autoclaved	0	0	3	0.018

[a] Samples were 60 ml of lake water with 0.6 g of nutrient broth (Difco) and 3 µCi of $^{203}Hg(NO_3)_2$. The ^{203}Hg concentration was increased 10-fold to enhance possible isotopic exchange.

[b] λ = 450 nm.

[c] MeHg, Methylmercury.

Table 2. Mercury methylation in the eastern and western basins of Clay Lake with their corresponding organic carbon and total mercury concentrations

		Lake water		Sediment-floc		
Location	Date	MeHg[a] produced (dpm/liter per day)	Total Hg concn (μg/liter)	MeHg produced (10^3 dpm/m^2 per day)	Total Hg concn (μg/g, dry wt)	Organic carbon (mg/g)
Eastern basin	17 April			UD[b]		
	14 May			2,046		
	5 June	UD		UD		
	14 June	UD	24	UD		
	27 and 28 June	512	14	320	2.5	
	10 and 11 July	314	27	168	1.9	19
	10 July	4,397[c]		52,956[c]		
	8 and 9 Aug.	UD	24	UD	1.6	34
	21 and 22 Aug.	1,176	25	331	1.7	25
	29 Aug.	UD	27	364	4.0	27
	5 Sept.	UD	32	320		
	11 Sept.	UD		43	2.4	20
	28 and 29 Sept.	UD	64	75		
Western basin	10 July	104,887[d]				
	11 Sept.			113		
	4 Oct.	UD, UD[d]		394	2.5	32

[a] MeHg, methylmercury.

[b] UD, Undetectable.

[c] Tryptic soy broth added.

[d] First number, quantity in epilimnion; second number, quantity in hypolimnion. In samples taken on 8, 21, and 29 August, mercury methylation was undetectable in both epilimnion and hypolimnion in the western basin.

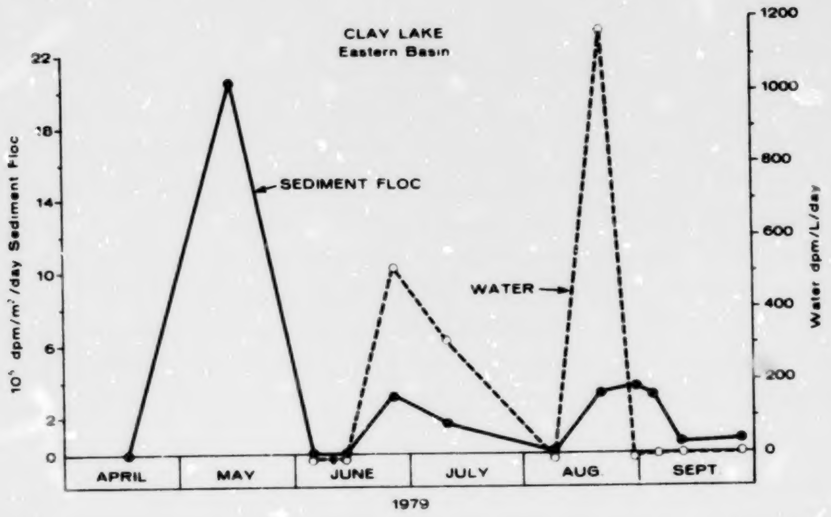

Fig. 1. Seasonal variation of methylmercury production in water column and sediment-floc samples.

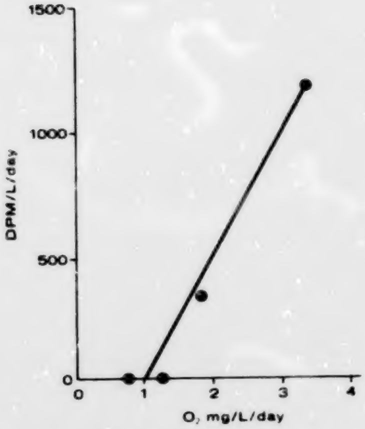

Fig. 2. Correlation between the oxygen consumption and the methylation activity in water column samples in the eastern basin of Clay Lake. r - 0.995; P 0.01.

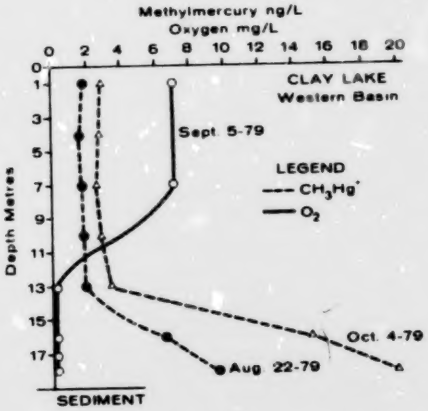

Fig. 3. Depth profiles demonstrating the increase in methylmercury concentration that occurred during a 6 week interval. There was no detectable methylation occurring in the water column during this period. The sediment-floc was actively methylating in the presence of sulfide.

7. MERCURY METHYLATION BY FISH INTESTINAL CONTENTS

John W.M. Rudd, Akira Furutani, and Michael A. Turner

ABSTRACT

A new radiochemical method has been applied to the examination of mercury methylation in fish intestinal contents. Intestinal contents of six freshwater fish species were found capable of converting $^{203}Hg^{2+}$ to $CH_3{}^{203}Hg^{+}$. This activity was observed in fish from five of six lakes tested whether or not there was mercury pollution. Bacterial activity in the intestinal contents is most likely resonsible for this methylation. Methylating activity of piscivors increased with decreasing quantity of intestinal contents. Generally, pike and walleye intestinal contents methylated a larger fraction of $^{203}Hg^{2+}$ than those of whitefish and suckers. These data contradict the previous general conclusion that there is no mercury methylation in fish.

INTRODUCTION

Microbial methylation of mercury has been recognized as a severe environmental problem for the past decade. Mercury methylation was first identified in the sediments of aquaria (11). Since that time it has been generally thought to occur only in the sediments of lakes and rivers. However, recently, in addition to sediments it has also been found to occur in the water column of a mercury-polluted lake (7).

It is also possible that methylation could occur inside fish. This could be a particularly important site because transfer to the muscle should then be easy. Pennacchioni et al. (18), however, found that mercury was not significantly methylated in vivo by fish tissues and organs.

A possible methylation site within fish is within the intestine. Jernelov (12) mentioned the occurrence of slow rates of mercury methylation in excised pike intestines, but no data were shown, and the importance of this observation was discounted. However, bacteria are known to be active in the intestines of some marine aquatic organisms and in fish (10, 26), so that there is a possibility that this is a site of significant mercury methylation. Since this site is so close to the fish tissue it could be particularly important to methyl mercury concentrations in fish muscle. This may be the case since Zanini et al. (27) have observed that inorganic mercury added to the diet of trout was later found methylated in the fish tissues and organs. Also Armstrong and Scott (2) have suggested that bioaccumulation of mercury from the water column of Ball Lake, Ontario, may be a significant contributor of mercury to fish tissues. Since the greater part of mercury in water is in the inorganic form, but that in the fish is nearly all present as methyl mercury, it is possible that methylation occurs within the fish intestinal tract, followed by translocation to the tissues and organs. During the summer of 1979, mercury methylation by fish intestinal contents was investigated as part of a larger project concerned with the severe mercury pollution problem of the Wabigoon River system of northwestern Ontario (7, 22). Fish samples were obtained from Clay Lake and Ball Lake, which are part of the Wabigoon River system (1), and from other nearby non-mercury-contaminated lakes. The observations and a discussion of their possible significance are presented below.

MATERIALS AND METHODS

The intestinal contents of the following species were examined for their ability to methylate mercury: northern pike, walleye, sauger, yellow perch, whitefish, cisco and sucker. Generally, pike, walleye, sauger, and perch are predators. Whitefish and cisco are zooplanktivors or bottom feeders. Suckers are primarily bottom feeders.

Fish samples were taken from Ball Lake and Clay Lake, which are severely contaminated by mercury. They were also obtained from mon-mercury-contaminated lakes, no. 239, 240, and 302 of the Experimental Lakes Area (6), and from Long Lake, which is within 3 km of Clay Lake but is not mercury contaminated.

Fish were caught in gill nets, which were tended at least every half hour since it was found that the fish voided as they struggled in the nets. The fish were killed by a blow to the head immediately after capture and stored on ice.

After the fish arrived at the field lab, their intestines were sealed by hemostats and excised close to the stomach and anus. The wet weight of intestinal contents was obtained by weighing the intestines before and after removing the contents. The method of handling the intestinal contents was adapted from methods developed for isolating strict anaerobic bacteria from rumen contents (9). These procedures were followed because strict anaerobic bacteria have been found to comprise a significant proportion of fish intestinal microflora (26). For time course incubations, to obtain a sufficiently large sample, the intestinal contents of four or five fish were removed without contact with air into a sterile glass reagent bottle that was being continuously flushed by nitrogen that had been deoxygenated by passage over hot copper oxide. An approximately equal quantity of filtered (0.45-μm pore size; Millipore) deoxygenated water was added to the pooled intestinal contents to enable the contents to be stirred and subsampled. The intestinal contents were homogenized by stirring. A 2-ml sample was withdrawn and frozen for later total mercury analysis (3). A further 2 ml of the sample was pipetted into the barrel of a sterile 50-ml all-glass syringe, which was continuously flushed by deoxygenated nitrogen. Usually 1.8 X 10^6 dpm of $^{203}Hg(NO_3)_2$ (New England Nuclear Corp.; ~ 1 mCi/mg) was added to the syringe before the plunger was put into the barrel. The syringe gas phase was then expelled, and zero time was recorded. Tests were done in duplicate for each point of a time course. Duplicate controls were establisned before injection of the label by addition of 1 ml of 4 N HCl to inhibit methylation. The samples and controls were incubated within 3°C of in situ temperature. After incubation the samples were also fixed by addition of HCl.

When intestinal contents from single fish were used, the subsampling, injection of label, and incubation procedures wre carried out in a similar manner as for the time course experiments.

The solvent extraction method described by Furutani and Kudo (7) was used to extract the $CH_3{}^{203}Hg^+$ produced during the incubation period. A 250-μl volume of the final benzene extract was added to 10 ml of PCS cocktail (Amersham) and counted in a Packard Tri-Carb scintillation counter.

The $CH_3{}^{203}Hg^+$ production is expressed as the fraction of label methylated per hour. The following equation was used for calculation: Fraction methylated per hour = $[(\text{net } CH_3Hg^+ \text{ dpm/g})/(Hg^{2+} \text{ dpm/g})]/(h \times D \times E_1 \times E_2 \times S)$, where dpm is disintegrations per minute, h is the hours incubation, D is the fraction of decay of the ^{203}Hg, E_1 is the efficiency of the scintillation counter, E_2 is th extraction efficiency of $CH_3{}^{203}Hg^+$, and S is the fraction of extracted sample counted. The fraction methylated was calculated as net counts in excess of the killed control.

A muscle sample was also taken from each fish and analyzed for total mercury concentration according to the method of Armstrong and Uthe (3).

Fish ages were estimated by the fin ray method of Beamish and Harvey (4) and Mills and Beamish (K.H. Mills and R.J. Beamish, Can. J. Fish. Aquat. Sci., in press).

RESULTS

Six examples of time course measurements of mercury methylation by fish intestinal contents are shown in Fig. 1. Intestinal contents of walleye and pike obtained from Clay Lake methylated mercury at easily detectable rates throughout the period of incubation. Sucker intestinal contents responded in a similar manner except that the methylation activity was somewhat slower than for other species taken from Clay Lake. Time course measurements were also done on pike from Long Lake and whitefish taken from Lake 302. Neither of these lakes has known sources of mercury contamination. In these cases mercury methylation either was absent or was not detectable until late in the incubation period. One Clay Lake sample, composed of equal quantities of pike and sauger intestinal contents, methylated mercury an order of magnitude faster than the other Clay Lake samples. This was the only time course experiment done early in the summer (11 July). All of the rest of the samples were taken after 28 August 1979.

A survey of methylating activity by intestinal contents from individual fish was carried out on several other lakes to see whether mercury methylation by fish intestinal contents was a common occurrence in other contaminated and non-contaminated lakes (Table 1). These data show that mercury methylation can occur at easily detectable rates in all species tested in both mercury-contaminated and non-contaminated systems. Thus the presence of mercury methylating enzymes or bacteria in fish intestines is not dependent on prior exposure to elevated mercury concentrations. Methylating activity by fish gut contents is evidently not a universal pheomenon, however, since very slow methylation or none was found in all species of fish taken from Long Lake (Fig. 1 and Table 1). However, the highest methylation rate in an individual fish occurred in a pike taken from Lake 239, which is not contaminated by mercury.

Variation in methylating activities (Table 1) represent fish-to-fish variation and not methodological problems since in the time course experiments the mean coefficient of variation of 10 duplicate samples was 10.6 ± 8.2%. Variation between individual fish of a species was as large as variations from lake to lake (Table 1).

DISCUSSION

The main purpose of this work was to establish whether methylation of mercury occurs in fish intestinal contents. This is clearly the case. Methylation occurred in gut contents of fish obtained from five of six lakes tested. It also occurred in all six of the species tested. In the literature there is frequent reference to a lack of methylating activity in fish intestines (e.g., references 8 and 16). The confusion seems to originate from the work of Pennacchioni et al. (18), who demonstrated that mercury was not methylated in vivo by fish tissues and organs. As part of their experimental design, Pennacchioni and co-workers fed fish large quantities of a bacterial antibiotic (Furazolidone). This would eliminate most microbial activity, and therefore their results pertain only to a lack of methylation by fish tissues and organs, not by microorganisms which inhabit the fish intestine.

Whereas the occurrence of methylating activity can be demonstrated, it is not possible to express the activity as an absolute rate (e.g., micromoles of CH_3Hg^+ per gram per hour) for two reasons: (i) the method is not a radiotracer method because ^{203}Hg was added as mercuric ion, which almost certainly did not come into equilibrium with the other mercury compartments of the sample during the incubation period (5); and (ii) the substrate (total mercury) concentration was approximately doubled by the cold carrier added to the samples. Consequently, methylating activities are expressed as the fraction of added label methylated per hour. This approach enables relative comparisons of methylating activity by individual fish and fish species. We think that this is a valid approach because of the progressive increases with time of the time course experiments, which indicate that sample-to-sample differences in $CH_3{}^{203}Hg^+$ content reflect relative differences in the quantities of $CH_3{}^{203}Hg^+$ produced during the incubation period. The good reproducibility of the method also indicates that samples react to addition of $^{203}Hg^{2+}$ in a predictable manner. A more detailed discussion of the present limitations of this method is given in the companion paper (7).

Because of the work of Pennacchioni et al. (18), who found no methylation when fish food contained antibiotics, and of Zanini et al. (27), who found methyl mercury in fish tissues fed inorganic mercury in the absence of antibiotics, it is probable that intestinal mercury methylation in fish is carried out by bacteria. This is true with respect to mercury methylation in the intestines of humans and rats (20, 21), although no methylating activity or methylating bacteria were found in rumen contents of sheep or cows (13).

No prior exposure to elevated mercury concentrations was necessary since methylation was detectable in the Experimental Lakes Area pike samples after only 4 h of incubation. The microbial ecology of fish intestines is not well understood. For example, there is still some controversy over whether fish have a resident intestinal flora or whether the bacteria present in the intestine are simply passing through with the food. Margolis (14) and Seki (23) concluded that there were no resident populations. However, Trust (25) found resident populations of between 10^6 and 10^8 bacteria per g in starved and fed Chum salmon, respectively. In addition, Trust et al. (26) identified several anaerobic species in intestinal contents, some of which appear to be peculiar to the fish intestine.

When fish methylating activity was plotted against the total wet weight of intestinal contents, species differences became apparent (Fig. 2). The fraction of mercury methylated per unit time by sucker intestinal contents appeared to be unrelated to the total weight of intestinal contents. Although there was not as wide a weight range for whitefish samples, there also appeared to be no relationship to sample size. In contrast, the pike samples showed increasing activity with decreasing sample size, and the single available walleye sample fell on the same line as the pike data (Fig. 2). These data suggest that something other than the quantity of food in the intestine was influencing the rate of methylation by the intestinal contents of the piscivorous species. This may have been the larger quantities of intestinal mucus found in the piscivorous species. It was observed that, unlike non-piscivorous samples, the smaller intestinal content samples from walleye and pike contained progressively larger proportions of intestinal mucus. The intestinal mucus is similar in many respects to the outer slime layer of fish, which has been found to be very active in the uptake and methylation of inorganic mercury (12, 15; unpublished data). The intestinal mucus of a wide variety of other species is known to be a site of intense bacterial activity (24). This observation may be of importance with respect to the contribution of intestinal mercury methylation to the concentration of mercury in the tissues of piscivorous fish, since inorganic mercury associated with the intestinal mucus would continue to be methylated in the absence of feeding.

There are several routes of entry of methyl mercury into fish. Olson et al. (17) have studied bioaccumulation through the gills and have compared this to methylation in the external slime of fish (12; unpublished data). Methyl mercury can also be bioaccumulated from ingested food, although only about 19% of the methyl mercury present in natural pike food is retained by the fish (19). However, 40 to 90% of the methyl mercury artificially added to food or administered directly to the fish gastrointestinal tract is assimilated (19). Thus unbound methyl mercury routinely produced in the intestinal contents or mucus, which would be equivalent to artificially administered methyl mercury, would be much more available for transport across the intestinal wall than natural methyl mercury in food. The relative importance of this methyl mercury as compared to other uptake routes is not known for fish living under field conditions. The availability of a radiochemical method which enables methylation to be detected in natural samples in short time periods will be a useful tool in attempts to answer this question.

ACKNOWLEDGMENTS

A. Lutz analyzed total mercury samples. B. Lamm kindly provided air transportation for some of the field work. R.D. Hamilton, F.A.J. Armstrong, J.F. Klaverkamp, and C. Kelly constructively discussed this manuscript. K. Mills and S. Chalanchuk aged fin ray samples.

This work was supported by the Freshwater Institute through the Canada Water Act, by the Inland Waters Directorate and by the Government of Ontario.

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Table 1. Results of survey of mercury methylation by fish intestinal contents

Lake[a]	Date (1979)	Species	Sample wt (g)	Fraction of ^{203}Hg methylated per h (X10^{-6})	Incubation time (h)	Muscle Hg (µg/g)	Fork length[b] (cm)	Wt (kg)	Age (yrs)
Clay	26 June	Pike	3.60	96	96	4.60	59	1.5	-[c]
	26 June	Perch	10.6[d]	58	96	1.30	20	0.2	-
	27 June	Walleye	~1[e]	177	96	3.30	37	0.6	-
	11 July	Sucker	7.00	95	40	-	29	0.4	-
	29 Aug.	Whitefish	0.36	49	25	2.01	49	2.6	12
		whitefish	0.36[f]	42	25	2.01	49	2.6	12
	5 Sept.	Whitefish	2.01	22	48	0.54	43	1.3	7
Long	11 Sept.	Sucker	1.00	ND	48	0.10	39	0.9	4
			1.00[f]	ND	48	0.10	39	0.9	4
			1.00	ND	48	0.08	-	0.9	6
		Cisco	0.43	ND	48	0.20	35	0.8	-
			0.43[f]	ND	48	0.20	35	0.8	-
Ball	23 Aug.	Whitefish	2.66	19	18	0.26	50	1.4	12
			1.09	10	18	0.42	48	1.5	13
		Pike	1.64	94	4	5.09	66	1.9	8
			15.5	50	4	3.48	61	1.6	9
		Sucker	9.60	3	38	2.60	45	1.7	23
			10.5	17	38	1.73	48	2.1	15
			0.78	23	38	0.84	45	1.5	13
302	23 Aug.	Whitefish	0.74	35	18	0.48	42	0.8	13
			2.09	17	18	0.29	37	0.6	13
			1.48	30	18	0.32	34	0.4	9
239	24 Aug.	Pike	3.29	47	4	0.49	69	2.4	5
			6.80	32	4	0.43	56	1.6	4
			4.92	32	4	0.40	59	1.4	7
			1.13	157	4	0.56	51	0.9	4
240	23 Aug.	Sucker	44.0	ND	38	0.56	51	2.0	18
			38.0	ND	38	0.63	45	1.4	17
			15.5	16	38	0.43	42	0.9	14
			10.5	2	38				

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[a] Ball and Clay Lakes are contaminated by mercury; Lakes 239, 240, and 302 and Long Lake are not mercury contaminated.

[b] Fork length, Length from the tip of the snout to the margin of the median rays of the tail fin.

[c] -, Not determined.

[d] Pooled intestinal contents of three perch.

[e] Pooled intestinal contents of seven walleye.

[f] Duplicate samples from one fish.

[g] ND, Not detectable.

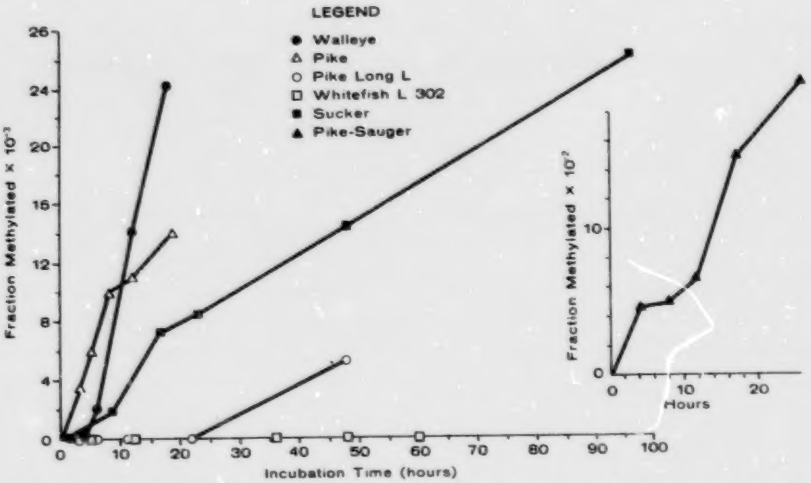

Fig. 1. Time course analyses of mercury methylation by intestinal contents of selected fish species. Unless shown otherwise, samples were taken from Clay Lake. The data are means of duplicate samples. Samples were composed of intestinal contents pooled from four or five individuals of each fish species.

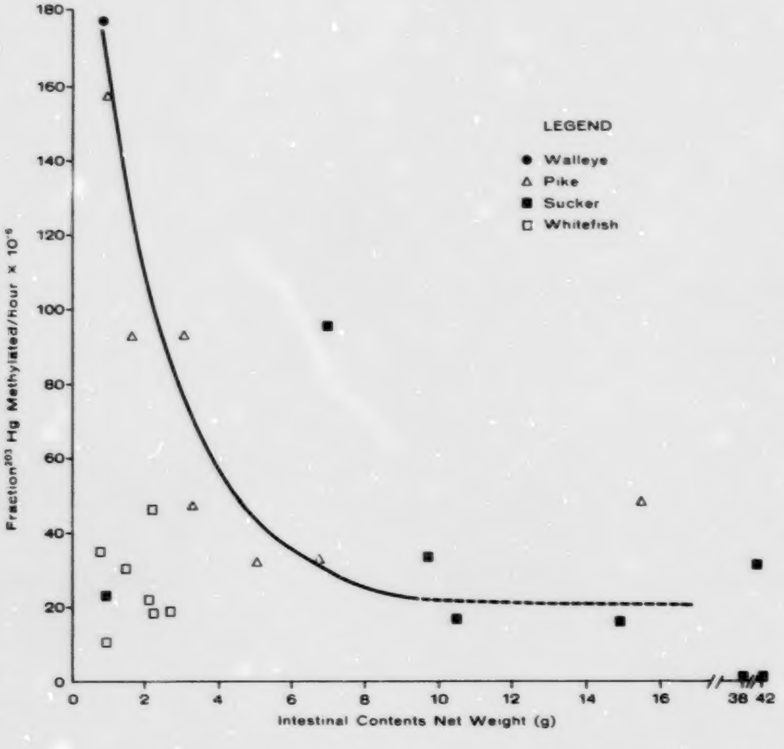

Fig. 2. Mercury methylation as a function of amount of intestinal contents of selected fish species.

8. SELENITE TOXICITY AND MERCURY-SELENIUM INTERACTIONS IN EMBRYONIC AND JUVENILE FISH

J. F. Klaverkamp, D. A. Hodgins, W. A. Macdonald, W. R. Lillie and A. Lutz

ABSTRACT

Acute lethal toxicities of selenium, toxic interactions between mercury and selenium in fertilized eggs, and selenium effects on mercury accumulation were determined in freshwater fish species. Selenite concentrations required to produce 50% mortality were approximately 29 mg Se/L in white sucker (*Catostomus commersoni*), 11 mg Se/L in northern pike (*Esox lucius*), and 5 mg Se/L in yellow perch (*Perca flavescens*) after 96, 75, and 240 hours of exposure, respectively. A marked synergistic effect between mercury and selenium toxicity in fertilized fish eggs reported by Huckabee and Griffith (1974) was not observed in eggs from rainbow trout (*Salmo gairdneri*) and lake trout (*Salvelinus namaycush*) in this study. Two approaches were used to determine effects of water-borne selenium on mercury concentrations in northern pike. In the first, a trend of reduced mercury contamination at a low selenium concentration (1 µg Se/L) with maintenance at control mercury contamination levels at a higher selenium concentration (100 µg Se/L) was apparent. In the second, a similar response of decreased $CH_3{}^{203}Hg$ accumulation in muscle-skin at lower selenium concentrations (1 and 10 µg Se/L), but maintenance at control accumulation levels at a higher selenium concentration (100 µg Se/L) was observed. Results and knowledge requirements are discussed with emphasis on relevance to increasing deposition rates of these chemical elements to freshwater ecosystems and using selenium to treat mercury-contaminated aquatic systems.

INTRODUCTION

Selenium enters aquatic environments by natural weathering processes (Bertine and Goldberg, 1971); combustion of fossil fuels (Weiss et al; Klein et al, 1975; Gutenmann et al., 1976); metal mining, smelting and refining (Demayo et al., 1979) and other industrial activities (Hashimoto, et al., 1970; Vokal-Borek, 1979). Recent estimates (Harriss and Hohenemser, 1978; Lantzy and Mackenzie, 1979) indicate that anthropogenic emissions are greater than natural sources in the transport of selenium to freshwater systems. In lakes selenium can be converted to methylated forms by microorganisms (Chau et al., 1976), and readily accumulates in fish (Adams and Johnson, 1977; Klaverkamp et al., 1982; Turner and Swick, 1982). Selenium toxicity studies, however, have only been conducted on a few fish species (Demayo et al., 1979; Hodson, 1982).

Interactions between selenium and mercury occur in many, diverse biological systems (Diplock, 1976; Nordberg et al., 1978) including fish (Kim et al., 1977; Sheline and Schmidt-Nielsen, 1977; Heisinger et al., 1979). While these interactions generally result in enhanced retention, but decreased toxicity, of each element in the presence of the other, two relevant exceptions have been reported in fish. First, a rare example of toxicity enhancement between selenium and mercury was seen in carp embryos exposed under laboratory conditions (Huckabee and Griffith, 1974). Second, inverse relationships between selenium and mercury concentrations were observed in fish exposed in the natural environment (Rudd et al., 1980; Speyer, 1980; Turner and Rudd, 1982). These recent field observations have led to suggestions that selenium has potential as a chemical amelioration measure in freshwater ecosystems contaminated by mercury (Rudd et al., 1980; Turner and Rudd, 1982). Additional research on these interactions in freshwater fish is required because mercury emissions from man's activities are greatly increasing deposition rates to freshwater ecosystems (Harriss and Hohenemser, 1978; National Academy of Sciences, 1978 and 1981).

The objectives of this study were to determine the acute lethal toxicity of selenium to white suckers (*Catostomus commersoni*), yellow perch (*Perca flavescens*) and northern pike (*Esox lucius*); to evaluate toxic interactions of selenium and mercury on rainbow trout (*Salmo gairdneri*) and lake trout (*Salvelinus namaycush*) embryos; and to assess the effects of selenium on mercury concentrations in northern pike.

MATERIALS AND METHODS

Acute lethal toxicity tests of selenite on northern pike, yellow perch and white suckers

Northern pike, *Esox lucius*, and yellow perch, *Perca flavescens*, were obtained from Clay Lake, a mercury polluted lake in northwestern Ontario (Jackson, 1980; Rudd et al., 1980), by using a 17 x 1.5 meter beach seine with 6.35 mm openings. White suckers, *Catastomus commersoni*, were obtained from Lake 384 in the Experimental Lakes Area (ELA) of northwestern Ontario (Brunskill and Schindler, 1971) by a commercial bait fisherman. This species is abundant in Clay Lake but juveniles could not be caught from the lake in sufficient numbers for toxicity testing. The Clay Lake fish were transported to ELA in continuously aerated Clay Lake water using an insulated, fiberglass container of about 900 liter capacity. Less than 5 percent mortality occurred during transportation.

All fish were acclimated without feeding for 3 to 6 days prior to testing in water from Lake 239 in the ELA at a flow rate of 2 to 4 liters per minute. This water was analysed (Stainton et al. 1974) on a monthly basis from May 16, 1979 to October 29, 1979, inclusive. Data, expressed as x ± S.D. (n = 7), are summarized as follows: Na, 1.36 mg/L ± 0.13; K, 0.72 mg/L ± 0.03; Mg, 0.82 mg/L ± 0.02; Ca, 2.74 mg ±0.13; pH, 6.37 ± 0.13; Conductivity, 29.57 µS/cm ± 1.05. From these means, a water hardness (Ca, Mg) value of 10.2 mg $CaCO_3$/L was calculated (APHA, 1971). Fish were held in continuously aerated water at a mean (± S.D.) temperature of 11.7°C ± 1.7 in 140 or 750 liter fiberglass tanks. All fish were held at a 12 hour light: 12 hour dark photoperiod.

A toxicity test was begun by distributing equal numbers of fish in a random manner into eleven 20 L polyethylene-lined, temperature-controlled test vessels. Prior to filling, the polyethylene liners were rinsed several times using Lake 239 diluent water. Temperature, dissolved oxygen, and pH of each test vessel were measured daily. Ten vessels contained selenium, added as sodium selenite, and one vessel contained Lake 239 diluent water as a control. A modified intermittent flow-through type of proportional diluter (Harrison et al., 1975) was used to maintain the 10 concentrations of selenite (A.K. Petro Chemical Ltd., Downsview, Ontario, analyzed at 102.7% Se and 98.0% Na) at a dilution factor of 0.75 and to deliver Lake 239 water to the control test vessel. Toxicity tests were conducted with continuous aeration and a 90 percent molecular replacement time of approximately 7.7 hours.

Ten white suckers, ten northern pike or seven yellow perch were exposed at each concentration. The mean loading densities were 1.36 gm/L/day for white suckers, 1.63 gm/L/day for northern pike and 0.57 gm/L/day for yellow perch. Test vessels were checked and dead fish removed on a logarithmic time series. Criterion for death was cessation of respiration. Fork length and weight were obtained from each dead fish. Concentrations producing death in 50% of the fish (LC_{50} values) were calculated according to the probit analysis method of Finney (1971). Median survival times and 95% confidence limits were calculated using the method of Litchfield (1949).

Water samples for determination of selenium concentrations were collected in 250 mL polypropylene bottles and acidified with 1 mL of concentrated nitric acid. These samples were kept at approximately 4.0°C until analyses could be completed. Portions were made to 30% acid with HCl and analyzed by a modification of the borohydride reduction method of Vijan and Wood (1976).

Toxic interactions of selenium and mercury on trout eggs:

Three experiments were conducted to determine toxic interactions of sodium selenite and mercuric chloride (Fisher) on fertilized eggs from rainbow trout (Salmo gairdneri) in experiments 1 and 2 and from lake trout (Salvelinus namaycush) in experiment 3. Exposures occurred under static conditions in polyethylene containers described in schematic manner in Fig. 1. Up to 40 exposure containers were supported in a temperature controlled water bath. Individual eggs in 1 cm x 1 cm chambers were supported by nylon mesh screening in an acrylic grid system of about eighty chambers (Fig. 1 - right panel) per container. Water aeration and circulation through the screen were continuously provided by an air lift located at the center of the chamber grid. Experimental designs and conditions for the three experiments are described in Table 1. Criteria for death were formation of white protein coagulate in chorionated embryos and immobility with cessation of heart rate in fry.

Water samples were analyzed for selenium content by atomic absorption spectrophotometry using techniques described in the previous section. For mercury analyses samples were collected in 250 ml Pyrex bottles which had been heated in a muffle furnace at 450°C overnight. Samples were preserved with addition of 3 ml conc HNO_3 and 1 ml 5% potassium dichromate. Portions were digested with permanganate and potassium persulfate (Kopp et al. 1972) and analyzed by flameless atomic absorption spectrometry (Armstrong and Uthe, 1971). Total ammonia concentrations in water samples from control (un-treated) containers at 360 and 576 hours of exposure were obtained using methods described by Stainton et al., 1974. Median survival times (MST) and median hatch times (MHT) were estimated by graphical interpolation on probit log plots of cumulative percent mortality against exposure time, except as noted in Results.

Effects of selenium on mercury bioconcentration in northern pike:

Two experiments were conducted to determine whether selenium added to water, as selenite, produced immediate and direct decreases in mercury accumulation in these fish. The first experiment was designed to establish whether sodium selenite had direct effects on mercury concentrations actually found in these fish. The second experiment evaluated the effects of sodium selenite pretreatment on ^{75}Se, ^{203}Hg and $CH_3{}^{203}Hg$ accumulation. For each experiment, northern pike were captured in Clay Lake by beach seine, were transported to the ELA, and were held, acclimated and exposed in ways described in the section on acute lethal toxicity tests.

In the first experiment 33 pike having a mean (± S.D.) length of 13.5 cm (± 1.3) and a mean (± S.D.) weight of 13.67 gm (± 3.89) were randomly distributed into eight polyethylene-lined 20 L test vessels previously described and were exposed in Lake 239 water for up to 12 days at a temperature of 11.1°C ± 0.1 and a photoperiod of 12:12 in selenite at nominal concentrations of 0, 1, 10 or 100 µgm Se/L. Nine fish were exposed to each concentration of 10 µg Se/L and 100 µg Se/L; 8 fish to 1 µg Se/L; and 7 fish were used as controls. The mean fish loading density was 1.02 gm per liter per day.

In this experiment, concentrations of mercury and selenium in northern pike carcass and liver were obtained to establish baseline levels and to determine the effects of selenite. Carcass was obtained by decapitation, evisceration and fin removal. Carcass, therefore, consisted largely of skeletal muscle and skin, but also included scales, spinal column and associated bones, nerves, systemic vasculature and lymphatic circulation. Whole liver was removed from the visceral contents and dissected free from the gall bladder. Carcass and liver samples were individually rinsed three times in distilled water, blotted on paper towels, placed in small plastic bags and frozen until analyses for mercury and selenium could be completed.

These samples were analyzed for selenium by digesting 0.5 g of sample overnight with 5 ml nitric and 1 ml perchloric acids and by heating to fuming perchloric, cooling, adding 7.5 ml conc. HCl, and bringing to 25 ml volume. Analyses were performed using the borohydride reduction method of Vijan and Wood (1976). For mercury analyses 0.5 g samples were digested with 5 ml of 4:1 $H_2SO_4:HNO_3$ and the addition of potassium permanganate. The digests were analyzed by the flameless atomic absorption method of Armstrong and Uthe (1971).

In the second experiment, 48 pike having a mean (± S.D.) length of 20.0 cm (± 2.6) and a mean (± S.D.) weight of 45.44 gm (± 18.19) were equally distributed in random manner into 8 plastic tubs each containing 40 liters of Lake 239 water under constant aeration. Before use each tub was acid-washed and rinsed at least 3 times with Lake 239 water. These tubs were placed in a temperature-controlled water bath. Pike were exposed at 12°C (± 0.4) and a photoperiod of 12:12 to sodium selenite concentrations of 0, 1, 10 or 100 µgm Se per liter for 3 days and then to radioactive ^{75}Se, ^{203}Hg or $CH_3{}^{203}Hg$ (New England Nuclear Ltd.) for seven days. The experimental design is presented in Table 2.

At the end of the exposure period, fish were anesthetized by adding 100 mg tricaine methane sulfonate (MS-222) per liter of water. Fork length and wet weight were obtained, and whole liver and muscle-skin samples were removed from each fish. The abdominal cavity was exposed by cutting the ventral surface with scissors from the vent to the heart cavity. Whole liver was removed, dissected free from the gall bladder, rinsed three times in distilled water, blotted on paper towels and weighed. After all visceral contents and the head with associated gill structures were removed, the left (anterior of fish facing away from person) half of the fish was removed by moving a scalpel along the spinal column. This "fillet" of skin and muscle (muscle-skin) without the spinal column was rinsed three times in distilled water, blotted on paper towels and weighed. Whole liver and muscle-skin samples were cut as necessary to fit in 50 x 9 mm plastic petri dishes for gamma counting on a lithium-drifted germanium detection system (Hesslein et al., 1980). Anterior portions of the muscle-skin samples were used for gamma detection if the entire sample was too large to fit into the petri dishes. The average per cent body weight of muscle-skin and whole liver samples were 15% and 0.8%, respectively.

In both experiments significant differences between selenium and mercury concentrations were determined using two-way analysis of variance, Duncan's multiple range test, and the t-test. In the second experiment homogeneity of variance was achieved by logarithmic transformation as recommended by Eberhardt (1975). These transformations can be converted to arithmetic mean values by the relationship of:

$$\log_{10} \frac{AM}{GM} = 1.1518\ S^2\ \frac{N-1}{N}$$

where AM = arithmetic mean; GM = geometric mean; S = the standard deviation of the logarithms in each sample; and N = the number in each sample (Ricker, 1975).

RESULTS

Figures 2, 3 and 4 present acute lethalities expressed as median survival times in the top panel and as median lethal concentrations (LC_{50}) in the bottom panel, of sodium selenite to northern pike, white sucker and yellow perch, respectively. Durations of exposure for determining median lethal concentrations varied because sensitivity to selenium was found to differ depending on species and possibly on fish loading density. Selenium concentrations required to produce 50 percent mortality ranged from approximately 5 mg Se/L at 240 hours of exposure for yellow perch to about 30 mg Se/L at 96 hours of exposure for white sucker. Table 3 presents a summary of these acute lethality studies by providing approximate median survival times at 30 mg Se/L and median lethal concentrations at given times.

Analytical chemistry data for water-borne mercury and selenium in the trout egg experiments are presented in Table 4. Mercury concentrations were extremely variable and generally much lower than expected. Selenium concentrations were generally less variable and nearer to those expected. In experiment 3 total ammonia concentrations were 410 µg N/L at 360 hours and 1250 µg N/L at 576 hours of exposure. These concentrations would provide un-ionized ammonia concentrations of 6 and 18 µg N/L, respectively, at 10°C and pH 7.9 (Trussel, 1972). These are acceptable levels according to Stephan (1975).

Table 5 presents values for MHT (left panel) and MST (right panel) for late-eyed stage eggs of rainbow trout exposed to mercury and selenium (Experiment 1, Table 1). The control (no added Hg or Se) was replicated four additional times. The percent coefficient of variation in MHT of eggs in these 5 controls was less than 8%, indicating good reproducibility. At mercury concentrations of 0.3 mg Hg/L and 1.0 mg Hg/L (Table 5 - left panel), there were decreases in MHT to approximately 58% and 66%, respectively, of control values. Most of the eggs did not hatch in 3 mg Hg/L and 10 mg Hg/L. Mercury at concentrations ranging from 0.3 mg Hg/L to 10 mg Hg/L produced a concentration-dependent decrease in MST (Table 5 - right panel). At the lower mercury concentrations of 0.3 mg Hg/L and 1.0 mg Hg/L, mortality occurred after the eggs had hatched. Selenium, at concentrations up to 10 mg Se/L, did not affect the mercury-induced inability to hatch, the decreases in MHT and the decreases in MST. Selenium alone had no effect on hatching time, and did not produce mortality.

In a second experiment (Experiment 2; Table 1), a different batch of rainbow trout eggs was exposed to the lower concentration range of mercury and selenium combinations used in Experiment 1. This was conducted in duplicate using dechlorinated Winnipeg city tap water (approximate hardness as Ca and Mg = 90 mg $CaCO_3$/L), with other experimental conditions similar to the first experiment (Table 1). Table 6 presents MHT and MST calculations obtained from Experiment 2. Mercury by itself produced a decrease in MHT at lower concentrations and mortality at higher concentrations. Selenium did not produce mortality and did not affect the mercury-induced decrease in MHT or mortality. While both of the mercury-induced effects were observed at approximately half an order of magnitude lower mercury concentrations than in experiment 1, the trends in these observations generally confirm those of experiment 1.

A third experiment was conducted using fertilized lake trout eggs (Experiment 3; Table 1). High concentrations (1, 10 and 20 mg Hg/L) of mercury produced mortality, but lower concentrations (0.01 and 0.1 mg Hg/L) did not decrease MHT as they did with rainbow trout eggs. Selenium at concentrations up to 50 mg Se/L had no effects on mercury-induced mortality, but at concentrations of 100 and 200 mg Se/L, selenite delayed mercury-induced (20 mg Hg/L) mortality by factors of 2.1 and 2.5, respectively. Selenium at 200 mg Se/L decreased MHT.

Table 7 presents data on mercury and selenium concentrations in carcass and liver of northern pike obtained from Clay Lake at three different times. Statistical analyses using the t-test indicated significant differences (Table 7) between fish length or weight and mercury contamination of the carcass. In other words, the smaller fish of batch 1 were significantly less contaminated by mercury than those in batches 2 and 3. After combining the data from the three batches of fish, linear regression analyses between carcass mercury concentration and length and between carcass mercury concentration and weight provided correlation coefficients of 0.76 and 0.73, respectively, which are significantly at $P \leq 0.001$. Linear regression analyses of these data between carcass mercury concentrations and condition factor (weight/fork length^3) provided a correlation coefficient of 0.20, which is not significant ($P > 0.2$).

In exposures of 3, 6 or 12 days, selenium at concentrations of 1, 10 or 100μgm/L did not produce pronounced, concentration-dependent decreases in mercury concentration of carcass, liver or liver-to-carcass ratios (Figure 5) from batch 3 northern pike (Table 7). Data analyses using Duncan's multiple range test indicated a biphasic relationship between mercury contamination of carcass and selenium concentration in water at day 12. A significant ($P \leq 0.05$) decrease in carcass mercury concentration was observed at the lowest selenium concentration, and a significant increase in mercury was seen at the highest selenium level. No significant influence on liver mercury concentrations by water-borne selenium was found over the 12 day exposure period.

The effects of selenium pretreatment on the accumulation of $CH_3{}^{203}Hg$, ^{203}Hg and ^{75}Se in muscle-skin and in whole liver of northern pike are presented in figures 6 and 7, respectively. The accumulation of $CH_3{}^{203}Hg$ in muscle-skin of these pike was significantly reduced by selenium at concentrations of 1 and 10 μg Se/L ($P \leq 0.1$ and 0.001, respectively) but was not affected by 100 μgm Se/L (Figure 6). Accumulation of ^{203}Hg in muscle-skin was not significantly affected by selenium pretreatment. Data on ^{75}Se accumulation were not pooled, since ^{75}Se accumulation was greater ($P \leq 0.001$) in fish exposed to radioactive inorganic mercury than in fish exposed to radioactive methyl mercury at the selenium pretreatment concentration of 100 μgm Se/L (Figure 6). No significant differences were observed in whole-liver accumulation of inorganic mercury and methyl mercury at different selenium pretreatment concentrations ranging from 1.0 to 100 μgm Se/L (Figure 7). Again, data of ^{75}Se accumulation were not pooled, since accumulation was greater in fish exposed to ^{203}Hg than in pike exposed to $CH_3{}^{203}Hg$ at selenium pretreatment concentration of 1.0 μgm Se/L.

DISCUSSION

Selenite toxicity occurs in northern pike, yellow perch and white sucker at concentrations similar to those for other freshwater fish species. Selenite concentrations required to produce 50 percent mortality ranged from approximately 5 mg Se/L for yellow perch after 240 hours of exposure to about 30 mg Se/L for white sucker after 96 hours of exposure. The 96-hour LC 50 values for selenite in other freshwater fish species are 8.1 mg/L for rainbow trout (Hodson et al., 1980); 14.3 mg/L for brook trout and 7.3 mg/L for juvenile fathead minnows (Cardwell et al., 1976); approximately 20 mg/L for zebrafish (Niimi and LaHam, 1976) and 35 mg/L for carp (Sato et al., 1980). Selenite is generally more toxic to early life history stages (Niimi and LaHam, 1975; Hodson et al., 1980), in hard water (Cardwell et al., 1976; Halter et al., 1980), and at higher temperatures (Ellis et al., 1937). Sub-lethal and chronic toxicity studies indicate that selenite produces behavioral impairment in fish at concentrations of 250 μgm/L (Weir and Hine, 1970); skin lessions (Cardwell et al., 1976) and blood dyscrasias (Hodson et al., 1980) occur at sublethal concentrations; chronic exposure to 100 μg Se/L, as selenite, is non-lethal to rainbow trout (Gissel-Nielsen and Gissel-Nielsen, 1978); invertebrates are more sensitive than fish (Halter et al., 1980); early life history stages of invertebrates are more sensitive than adults (Schultz et al., 1980); and algal growth is reduced at concentrations as low as 50 μgm/L (Hutchinson, 1973). In the natural environment, fish mortality has occured from accumulation of selenium through an aquatic food chain (Barnhart, 1958). More information on selenium toxicology to fish and other aquatic organisms can be found in recent reviews (Demayo et al., 1979; Hodson, 1982; Turner and Rudd, 1982).

The marked synergistic effect between mercury and selenium described for carp eggs (Huckabee and Griffith, 1974) was not observed in this study on eggs from rainbow trout and lake trout. Mercury toxicity to these trout eggs was evident as decreased median hatch and median survival times at approximately the same concentrations as in carp eggs, however, selenium did not influence mercury toxicity unless a concentration of 100 mg Se/L or higher was employed. There were major differences in experimental procedures between the investigation on carp eggs and this study. For example, investigations on carp eggs were conducted over the entire embryological period of development, at temperatures which were higher by 10 to 17°C, and on eggs which were fertilized in a saline solution. It is interesting to note that preliminary studies in our laboratory suggest that selenium but not mercury, accumulation in lake trout eggs depends upon ionic strength of the solution surrounding the eggs. Biological factors, such as species differences and permeability differences in primary envelope or vitelline membrane, may also be responsible for the different observations between carp and these salmonids. Additional research on processes of mercury selenium transport and toxicology is required to understand these differences.

Direct effects of waterborne selenium on mercury concentrations in Clay Lake pike were investigated using two approaches. These were chosen to investigate whether selenium could reduce mercury accumulation in Clay Lake pike by increasing mercury elimination or by inhibiting mercury uptake. In the first approach, effects of selenium on mercury elimination were determined by measuring carcass mercury concentrations (Fig. 5 - top panel) and by evaluating mercury clearance processes using liver/carcass ratios (Fig. 5 - bottom panel) as modified from Jernelov and Lann (1971). A trend toward a biphasic response with mercury contamination being reduced at low selenium concentrations (1 μg Se/L) but being maintained at control levels at high selenium concentrations (100 μg Se/L) was observed. The validity of this trend should be tested by additional research using larger sample sizes and longer exposure times. In the second approach, radioactive isotopes of inorganic and organic mercury were used to evaluate the effects of selenium pretreatment on mercury and selenium uptake (Figs. 6 and 7). In muscle-skin another biphasic response of decreased methyl mercury accumulation at lower selenium concentrations, but maintenance at control levels at higher selenium concentrations was observed. Variability in accumulation of inorganic mercury in muscle-skin was decreased in the presence of added selenium, and a trend toward elevated inorganic mercury accumulation was observed at all selenium concentrations. No consistent pattern was observed in the accumulation of ^{75}Se in the presence of ^{203}Hg and $CH_3{}^{203}$Hg. Direct uptake of selenium from water is not limited by concentrations of 100 μg Se/L or less, since these concentrations did not reduce the accumulation of ^{75}Se in muscle-skin and liver.

Other investigators have also reported biphasic interactions between selenium and mercury accumulation in fish or an enhancement effect of selenium on mercury accumulation. In the northern creek chub (Semotilus atromaculatus) selenium produced increased whole-body accumulation of mercury at relatively low mercury concentrations and decreased mercury accumulation at higher toxic concentrations (Kim et al., 1977). In goldfish (Carassius auratus) selenium administration produced increased whole body accumulation of mercury with maximum mercury binding occurring at approximately equimolar concentrations of Hg and Se

(Heisinger et al., 1979). Compartments of these goldfish containing skeletal muscles also had elevated mercury in the presence of selenium. Substantial increases in methyl mercury concentrations in skeletal muscle of killifish (Fundulus heteroclitus) were produced by selenium at body burden concentrations of approximately 0.9 mg/Kg body weight (Sheline and Schmidt-Nielsen, 1977). In general, these laboratory observations contradict field studies on fish (Rudd et al., 1980; Speyer, 1980) which show decreased mercury accumulation in the presence of elevated selenium concentrations. Recent investigations have shown that food is an important route of uptake for selenium's effect of decreasing mercury accumulation in these studies (Turner and Swick, 1982) and that a selenium biotransformation process, probably not at the primary productivity level (Rudd and Turner, 1982), is necessary for the accumulation of Se (Rudd et al., 1980). It is apparent that interactions in the accumulation of these chemical elements by fish are complex and cannot be determined solely by acute exposures to water-born selenium.

Investigations using birds and mammals also demonstrate complex interactions in the accumulation and distribution of mercury and selenium, and should be considered since some of these animals are fish consumers. The accumulation in these animals of Hg and Se is dependent on many factors; for example, the molar ratio (Moffitt and Clary, 1974; Hansen and Kristensen 1979); dose (Magos and Webb, 1976; Kristensen and Hansen, 1979) sequence of administration (Parizek et al., 1971; Chmielnicka et al., 1979); physiological organ system (Growth et al., 1972; Komsta-Szumska and Chmielnicka, 1977); nutritional status (Ohi et al., 1976; Burk et al., 1977); sex (Stoewsand et al., 1974); route of administration (Groth et al., 1972; Fang, 1977; Hansen and Kristensen, 1979) and species (Eaton et al., 1980). Fundamental investigations on factors such as these and on environmental conditions in the field are required to understand processes controlling mercury and selenium interactions in fish.

Mercury contamination of small Clay Lake pike increased with increased length and weight (Table 7). Larger pike, however, from Clay Lake and other mercury-contaminated systems having controlled discharges show decreased levels of mercury with increased length (Olsson, 1976) and weight (Armstrong and Scott, 1979). The increased contamination in small fish may be due to increased uptake by these voracious omnivores during a period of very intensive feeding, to selective feeding of highly contaminated organisms by the smaller fish, to increased absorption of mercury by gills, gut or other route of uptake, to depressed mercury excretory systems in these fish, or to some combination of these factors. Whatever the cause(s) may be, it is apparent that mercury contamination of Clay Lake pike is continuing in spite of reduced discharges.

Selenium addition to mercury-contaminated freshwater ecosystems, such as Clay Lake, may have beneficial effects in reducing mercury concentrations in fish and other aquatic biota and in antagonizing mercury toxicity to fish and their consumers (Rudd et al., 1980; Turner and Rudd, 1982). If added as selenite, the most feasible form in terms of cost (Turner and Rudd, 1982), chemical and biological transformations would probably occur resulting in other inorganic species (Demayo et al., 1979) methylated forms (Chau et al., 1976; Niimi and LaHam, 1976), selenium-lipid complexes (Schwarz and Pathak, 1976), or in selenoamino acids and proteins (Ganther, 1974). Identification, quantification and toxicity testing of actual transformation products would be essential if concentrations increased in the water or bioaccumulated through the food chain. Research on chemical equilibrium dynamics and toxicology of selenium in freshwater systems and on processes previously discussed in selenium and mercury interactions in aquatic biological sytems would also contribute to understanding the impact of mercury and selenium from atmospheric fallout (N.A.S., 1981) on these aquatic systems.

ACKNOWLEDGMENTS

We express sincere appreciation and gratitude to Robert Corbett, David Duncan, Helve Hobe and Judy Klaverkamp for technical assistance, Brigitte deMarch for advice on statistical analyses, Grace Decterow and Lesley McIver for typing all manuscript drafts, and Laurie Taite for preparing the graphic illustrations. The constructive reviews of F.A.J. Armstrong, P. Campbell, R.D. Hamilton, S.G. Lawrence, J.W.M. Rudd, M.A. Turner, and R. Wagemann greatly improved the manuscript quality.

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Table 1. Experimental designs and conditions for investigations on toxic interaction of selenium and mercury on fertilized trout eggs.

	Experiment		
	1	2	3
Design	6^2 factorial; nominal Hg and Se concentrations of 0, 0.1, 0.3, 1.0, 3.0 and 10 mg element/L.	4^2 factorial; nominal Hg and Se concentrations of 0, 0.1, 0.3 and 1.0 mg element/L.	4^2 factorial set with nominal Hg and Se concentrations of 0, 0.01, 0.1, 1.0 and 10 mg element/L and a 2^2 factorial set with 0 and 20 mg Hg/L and with 10, 20, 50, 100 and 200 mg Se/L.
Fish species	rainbow trout	rainbow trout	lake trout
Stage of egg development	late eyed	late eyed	early eyed
No. of egg container	25	25	20
No. of containers/concentration	1 (4 extra controls)	2	1
Temperature(°C)	13-16	8.5-10.0	9.9-10.3
pH	6.10-6.55 (n=39)	7.79-7.89 (n=39)	-
Water source	L239; E.L.A.	U.V. dechlorinated Winnipeg city tap water	U.V. dechlorinated Winnipeg city tap water.
Frequency of water changes	every 48 hours	every 48 hours	not changed
Duration of exposure	120.5 hours	184 hours	576 hours
Observation intervals	ranged from 2 to 24 hour intervals	every 8 hours	every 12 hours

Table 2. Design of experiment to investigate effects of sodium selenite on accumulation of radio-labelled isotopes, Se^{75}, Hg^{203} and $CH_3Hg^{203}m$ in northern pike.

Exposure Vessel No. (40 liters ea.,6 fish per vessel)	Selenium Pre-treatment[a] (expressed as concentration of Se in μg/L)	Radio-labelled Isotope[b] (μC per exposure vessel)		
		Se^{75}	Hg^{203}	CH_3Hg^{203}
1	100	4	-	8
2	100	4	10	-
3	10	4	-	8
4	10	4	10	-
5	1	4	-	8
6	1	4	10	-
7	-	4	-	8
8	-	4	20	-

[a] = Pretreatment exposure period was 3 days.

[b] = Isotope exposure period was 7 days after pretreatment exposure period.

Table 3. Summary of acute lethality studies on northern pike, yellow perch and white sucker.

Species	Median Survival Time (hours) at 30 mg Se/L	Median Lethal Concentration (mg Se/L)
Northern pike	6.5	11.1 at 75.5 hours
Yellow perch	41	4.8 at 240 hours
White sucker	75	29 at 96 hours

Table 4. Chemical analyses of water-borne mercury and selenium in experiments on toxic interactions in fertilized trout eggs

EXPERIMENT 1[a]			EXPERIMENT 2[a]			EXPERIMENT 3[b]		
			Mercury Concentrations (mg/L)					
Expected	Actual	% Expected	Expected	Actual	% Expected	Expected	Actual	% Expected
			0	0.0038	-			
0.1	0.013	13	0	0.0003	-	0.01	0.0052	52
0.1	0.020	20	0.1	0.0094	9	0.1	0.014	14
0.3	0.028	9	0.1	0.050	50	1.0	0.059	6
1.0	0.39	39	0.3	0.130	43	10.0	5.64	56
3.0	1.94	65	0.3	0.120	40	10.0	5.98	60
3.0	1.36	45	0.3	0.360	120	20.0	14.6	73
10.0	4.15	42	1.0	0.710	71			
10.0	4.02	40	1.0	0.460	46			
			1.0	0.850	85			
			Selenium Concentrations (mg/L)					
Expected	Actual	% Expected	Expected	Actual	% Expected	Expected	Actual	% Expected
0.1	0.1	100	0	<0.0005	-	0.01	0.005	-
0.3	0.33	110	0	<0.0005	-	0.1	0.11	110
0.3	0.33	110	0.1	0.086	86	1.0	0.96	96
0.3	0.27	90	0.1	0.110	110	10.0	10.0	100
1.0	1.0	100	0.3	0.30	100	20.0	20.0	100
1.0	0.55	55	0.3	0.34	113	50.0	53.0	106
10.0	8.1	81	1.0	1.05	105	100.0	110.0	110
10.0	7.6	76	1.0	1.05	105	200.0	200.0	100

a = Water samples were taken at the end of 48 hour exposure periods.

b = Water samples were taken at the end of 24 hour exposure periods.

Table 5. Median hatch times and median survival times of fertilized rainbow trout eggs in late eyed stage of development exposed to combinations of mercury and selenium. Experimental design and conditions are described under Experiment 1 in Table 1.

	Median Hatch Time (hours) Mercury Concentration (mg Hg/L)							Median Survival Time (hours) Mercury Concentration (mg Hg/L)					
Selenium Concentration (mg Se/L)	0	0.1	0.3	1.0	3.0	10.0		0	0.1	0.3	1.0	3.0	10.0
0	77	71	45	51	N.H.	N.H.	0	N.M.	N.M.	115	107	68	12
0.1	82	76	40	32	N.H.	N.H.	0.1	N.M.	N.M.	115	95	111	14
0.3	76	72	45	45	76	N.H.	0.3	N.M.	N.M.	96	107	84	13
1.0	76	76	44	61	N.H.	N.H.	1.0	N.M.	N.M.	96	98	78	17
3.0	73	75	55	56	100	N.H.	3.0	N.M.	N.M.	128	110	96	19
10.0	71	72	67	61	N.H.	N.H.	10.0	N.M.	N.M.	175*	133*	107	26

N.H. = no hatch N.M. - no mortality * by extrapolation beyond experiment duration

Table 6. Median hatch times and median survival times of fertilized rainbow trout eggs in late eyed stage of development exposed to combinations of mercury and selenium. Values are the means of duplicate exposures. Experimental design and conditions are described under Experiment 2 in Table 1.

	Median Hatch Time (hours) Mercury Concentration (mg Hg/L)					Median Survival Time (hours) Mercury Concentration (mg Hg/L)			
Selenium Concentration (mg Se/L)	0	0.1	0.3	1.0	Selenium Concentration (mg Se/L)	0	0.1	0.3	1.0
0	175	150	102	>178	0	N.M.	N.M.	97	102
0.1	175	151	101	>178	0.1	N.M.	N.M.	111	121
0.3	173	144	92	>178	0.3	N.M.	N.M.	111	119
1.0	171	152	115	>102	1.0	N.M.	N.M.	115	109

N.M. = no mortality

Table 7. Concentrations of mercury and selenium in carcass and liver of northern pike from Clay Lake, Ontario.

	Pike Batch Number (capture date; no. of samples)		
	1 (July 26, 1979; n=14)	2 (Aug. 8, 1979; n=8)	3 (Aug. 23, 1979; n=10)
Carcass [Hg] (μgm/gm)	0.70 ± 0.12[a]	1.04 ± 0.07	0.92 ± 0.25
Liver [Hg] (μgm/gm)	1.05 ± 0.20	1.17 ± 0.19	1.52 ± 0.51
Liver/Carcass Ratio [Hg]	1.53 ± 0.20	1.13 ± 0.15	1.71 ± 0.75
Carcass [Se] (μgm/gm)	0.17 ± 0.04	0.12 ± 0.02	N/A
Liver [Se] (μgm/gm)	0.79 ± 0.21	0.99 ± 0.20	N/A
Liver/Carcass Ratio [Se]	4.91 ± 1.30	8.21 ± 1.52	-
Fork length (cm)	14.4 ± 2.4[a]	19.4 ± 1.7	17.4 ± 3.1
Weight (gm)	19.49 ± 9.23[b]	44.49 ± 9.13	36.78 ±21.73

Data are expressed as mean and one standard deviation

N/A = not analyzed
a = significantly less at $P \leq 0.01$ than batch 2 and 3.
b = significantly less at $P \leq 0.05$ than batch 2 and 3.

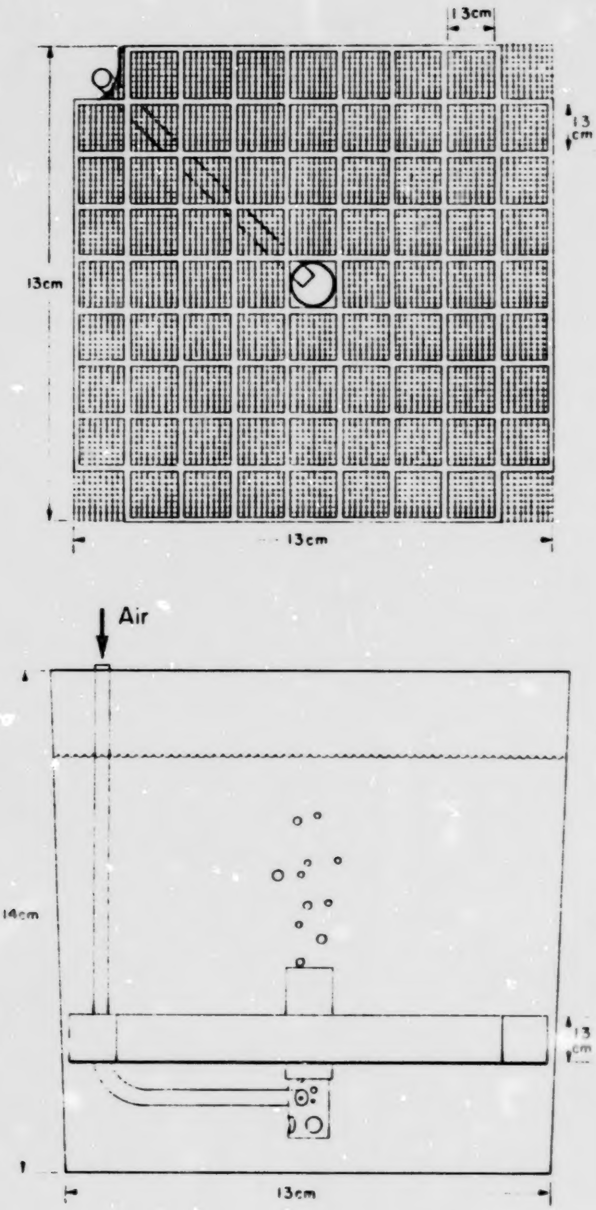
1 3cm
1 3 cm
13cm
13cm
Air
14cm
1 3 cm
13cm

Fig. 1. A schematic representation of exposure container used in fish egg experiments. Lower panel presents side view and upper panel presents top view.

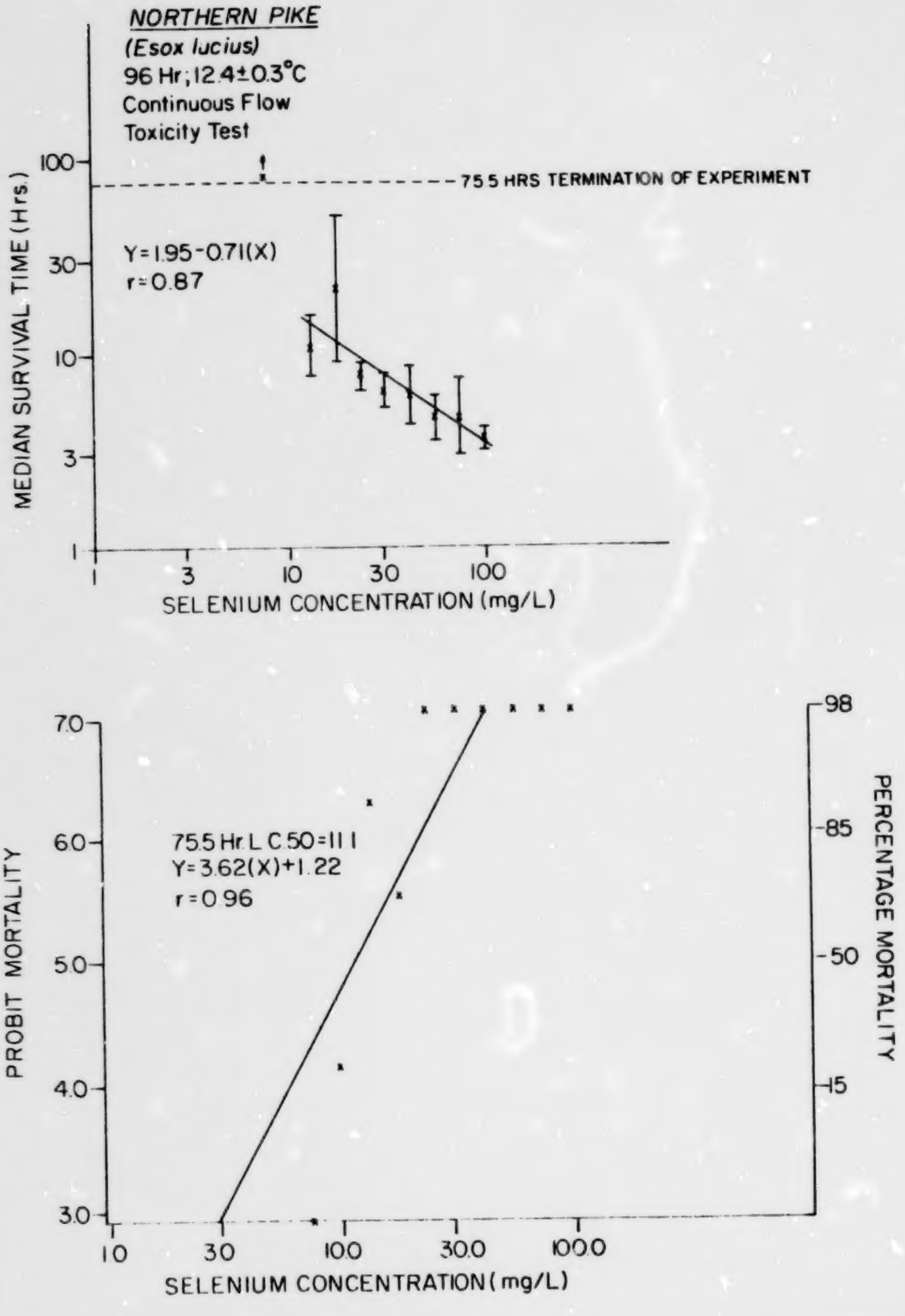

Fig. 2. Median-survival-time (top panel) and lethal response (bottom panel) curves for northern pike exposed to sodium selenite. Regression equations are expressed in log units for Se concentrations and median survival time values.

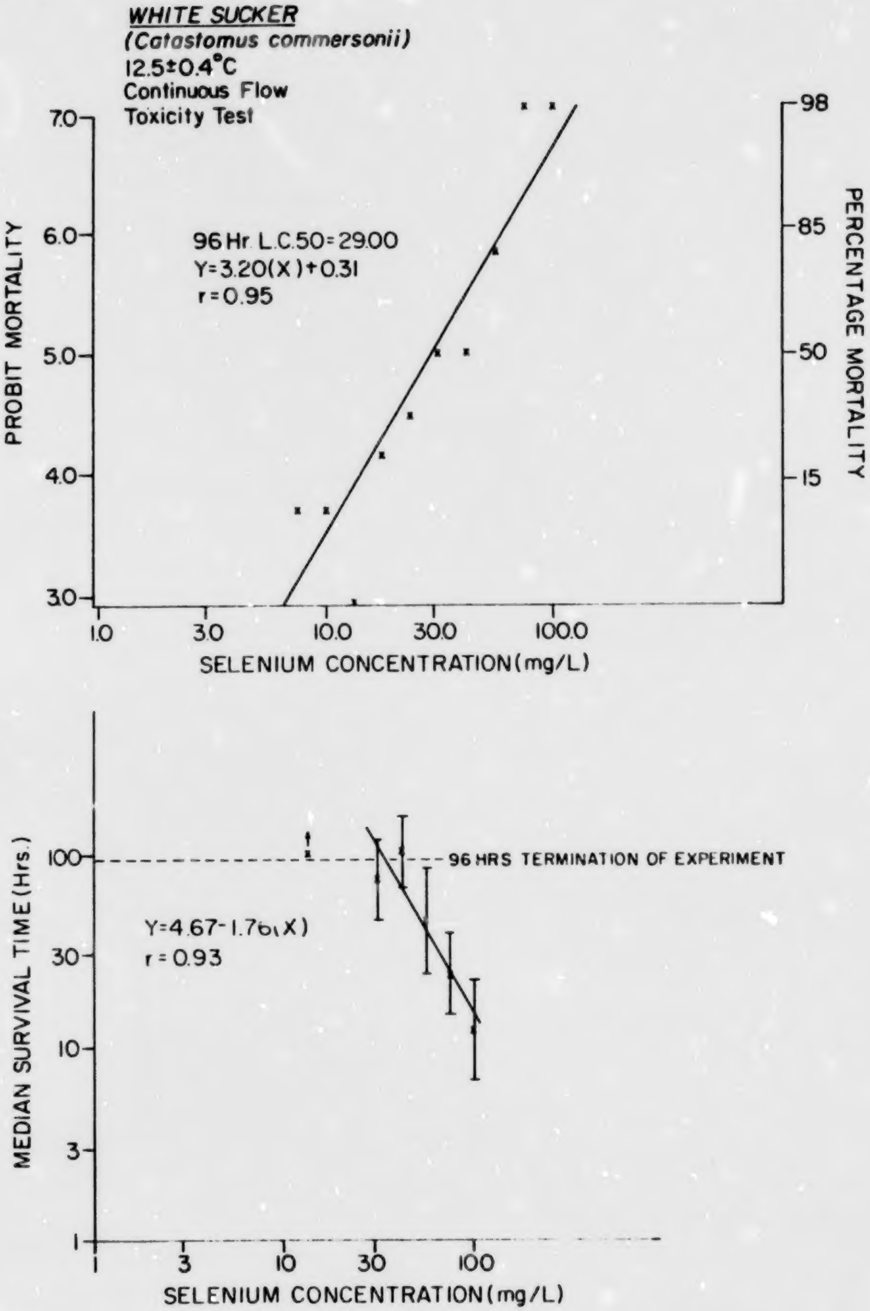

Fig. 3. Median survival-time (top panel) and lethal response (bottom panel) curves for white suckers exposed to sodium selenite. Regression equations are expressed as in Fig. 2.

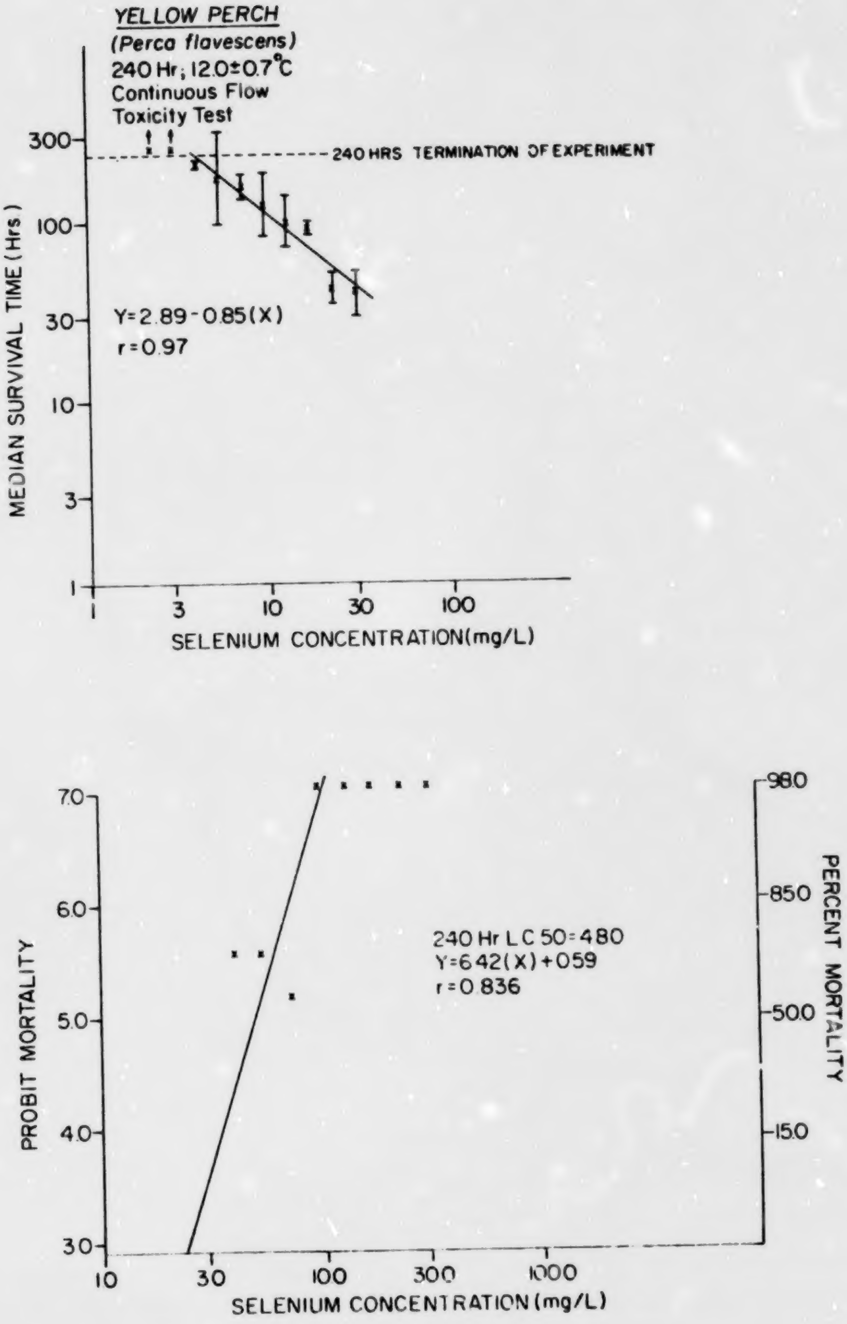

Fig. 4. Median survival-time (top panel) and lethal response (bottom panel) curves for yellow perch exposed to sodium selenite. Regression equations are expressed as in Fig. 2.

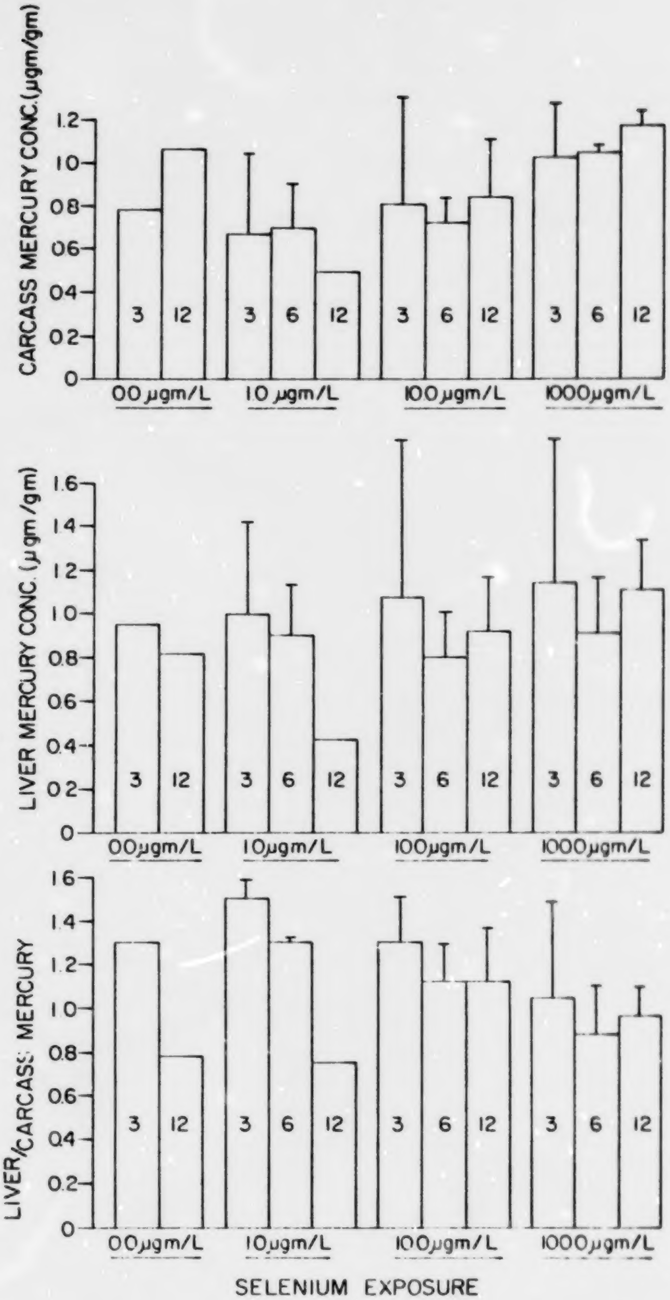

Fig. 5. Effects of selenium on mercury concentration in Clay Lake northern pike carcass (top panel), liver (middle panel) and liver-to-carcass ratios of mercury concentrations (bottom panel). Vertical lines represent one standard deviation. Each value is the mean of two (no standard deviation) or three (includes standard deviation) fish. Numbers in the histograms represent days of exposure at selenium concentrations indicated along the horizontal axis.

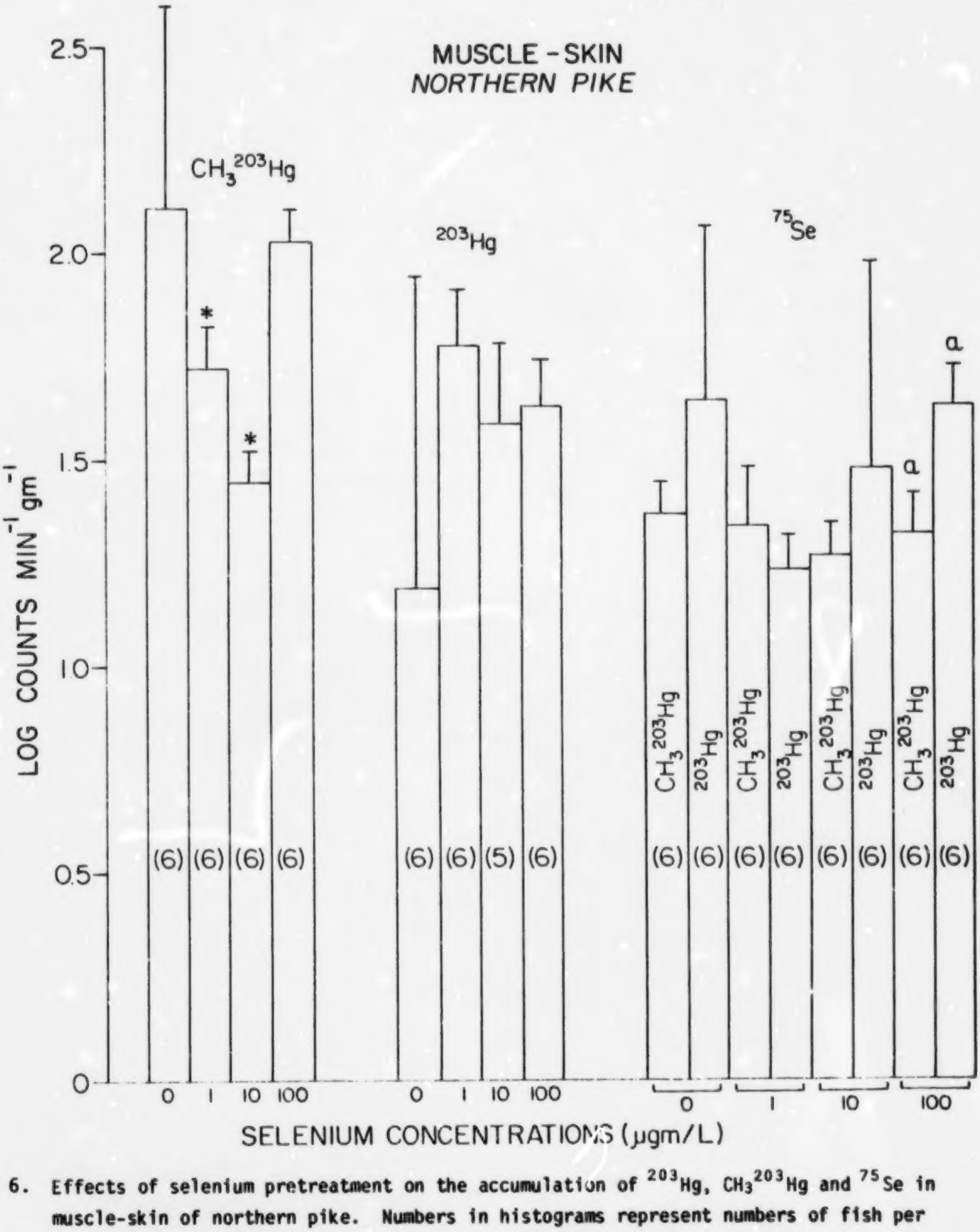

Fig. 6. Effects of selenium pretreatment on the accumulation of ^{203}Hg, $CH_3{}^{203}Hg$ and ^{75}Se in muscle-skin of northern pike. Numbers in histograms represent numbers of fish per treatment at selenium concentrations indicated along the horizontal axis. * = data are significantly different from selenium untreated fish at $P \leq 0.1$ for 1 μgm Se/L and at $P \leq 0.001$ for 10 μgm Se/L. a = data are significantly different from each other at $P \leq 0.001$.

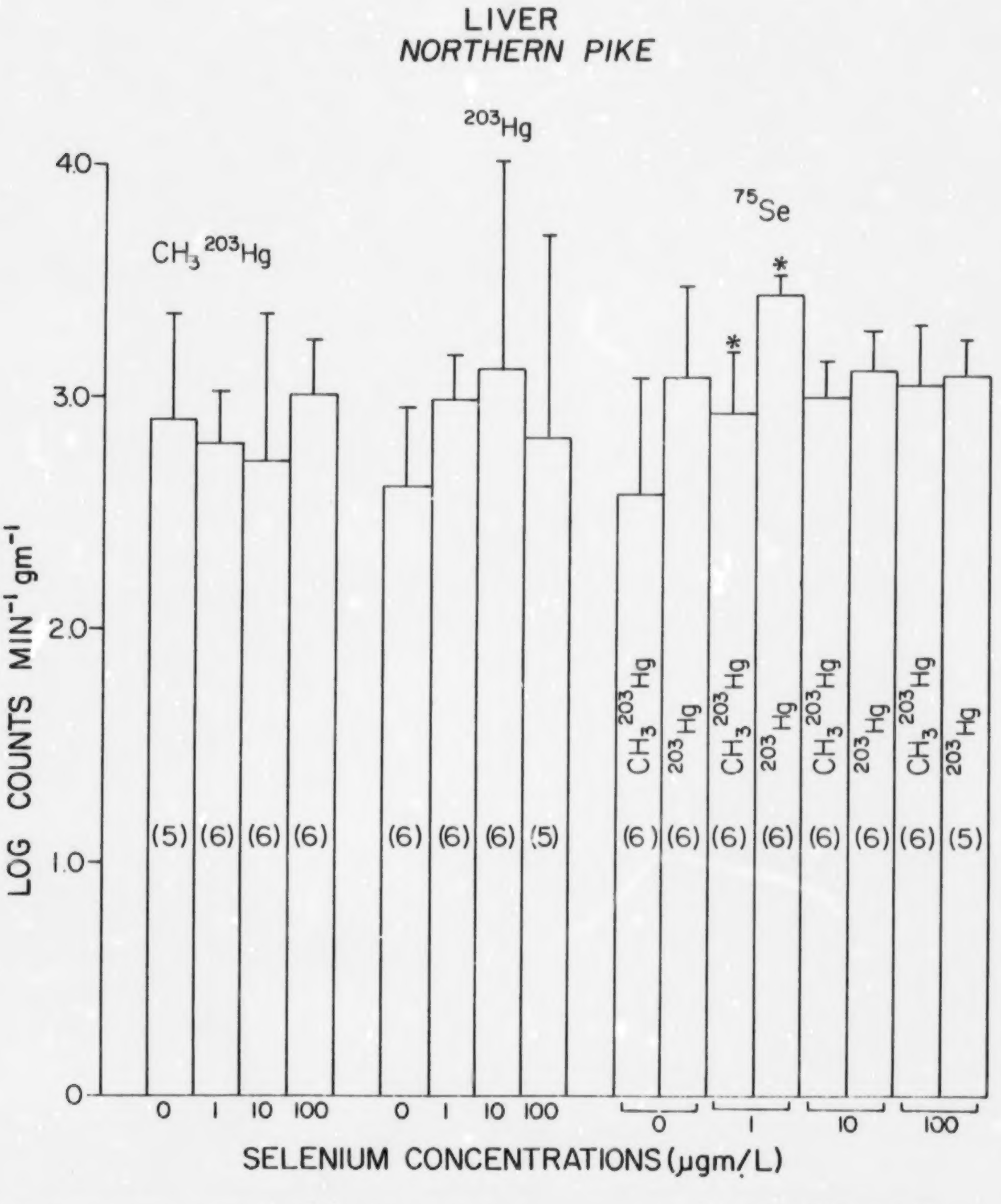

Fig. 7. Effects of selenium pretreatment on the accumulation of ^{203}Hg, $CH_3{}^{203}Hg$ and ^{75}Se in liver of northern pike. Numbers in histograms represent numbers of fish per treatment at selenium concentrations indicated along the horizontal axis. * = data are significantly different from each other at $P \leq 0.05$.